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VOL. 13, SEC. A. NOVEMBER, 1935 NUMBER 5

A NOTE ON THE SPECTROSCOPIC DETERMINATION OF THE VITAMIN A CONTENT OF PILCHARD OIL[1]

BY G. M. SHRUM[2] AND THOMAS G. HOW[3]

Abstract

An attempt has been made to measure spectroscopically the Vitamin A content of pilchard oil. Using the same conversion factor as for cod liver oil, measurements of the extinction coefficient at 3280Å gave Vitamin A values much larger than those obtained by biological tests. It has been shown that this discrepancy cannot be wholly ascribed to either the coloring matter or the saponifiable material in the oil. A satisfactory check on the results can be obtained only when it is possible to remove completely the Vitamin A from the oil, without otherwise modifying it.

Introduction

It has been fairly well established that Vitamin A concentrates and oils of high Vitamin A potency give a constant ratio among the results of the biological, chemical and physical methods for the determination of the Vitamin A content (2, 3, 6). Since spectroscopic measurements are relatively easy to make and at the same time tend to give the highest degree of accuracy (7), it seemed worth while to try to extend this method to measurements of the Vitamin A content of lower potency oils. This report deals chiefly with such an attempt, the oil under investigation being British Columbia pilchard oil. Some preliminary results are given to indicate the possibilities of the method. A more extended analysis can be made only when a greater number of biologically tested samples are available.

For high potency oils the Vitamin A content in 1934 International Vitamin A units can be obtained from the extinction coefficient at 3280Å by using a suitable conversion factor. The extinction coefficient, k, is defined by the equation $I = I_0 10^{-kx}$, where I_0 is the light incident on the absorbing solution and I that which is transmitted through x cm. of the solution. The value of this coefficient at 3280°A was determined by a visual method, using a fluorescent screen, and also photographically. Where it was necessary to obtain k for different wave-lengths, absorption spectra were obtained with the use of a step-sector and a quartz spectrograph.

Experimental

The most convenient method for determining k was found to be the visual method. It included the use of a copper arc, a filter which transmitted a narrow band at 3280Å, a fluorescent screen and some mechanism for con-

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trolling the intensity of the incident light. Such a method has been developed by Adam Hilger, Ltd., and the apparatus named a "Vitameter A." An instrument somewhat similar in design was constructed and used in this work. While, in the "Vitameter A," a cylindrical lens and rectangular aperture are used for adjusting the intensity, in this instrument the variation in intensity is controlled by an adjustable sector. The instrument is shown in diagram in Fig. 1. A is a copper arc run at 3 amp. on a d-c. circuit of 110 volts; B_1

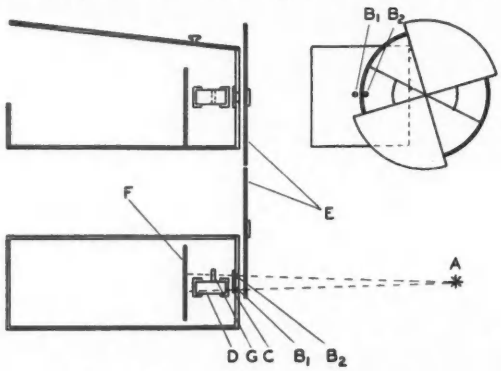

FIG. 1. *Arrangement of the apparatus for visual spectrophotometry at 3280Å. A, copper arc; B_1, B_2, circular apertures; C, a silvered quartz filter; D, cell for the solution; E, an adjustable sector; F, a fluorescent screen of uranium glass; G, a compensating glass plate.*

and B_2 are two small circular apertures; C is a light filter consisting of a silvered quartz window which transmits a narrow band of radiation at 3280Å (9); D is a cell containing the solution under examination; E is an adjustable sector; F is a fluorescent screen of canary glass. A compensating glass plate, G, is placed in the beam which does not pass through the solution. By varying the adjustable sector the intensity of the light passing through B_2 can be varied, and the two images at F can thus be brought to the same brightness. From the angular setting of the sector, $\log \frac{I_0}{I}$ can be found, and hence k. The sector was run at a speed of 30 rev. per sec., sufficiently fast so that there was no flicker. Talbot's law, which states that, "the apparent intensity of an intermittent light is proportional to the time of each individual flash, provided there is no flicker," would then hold.

The order of accuracy of such a determination can best be shown by graph A, Fig. 2, plotted to illustrate Beer's law, which postulates a linear relation between extinction coefficient and concentration. The concentration is given in terms of the number of grams of oil per 100 gm. of the cyclohexane which was used as solvent. Values of $\log \frac{I_0}{I}$ plotted on the graph were average values of five readings which seldom deviated more than 5% from the mean. This visual method was checked by finding k photographically,

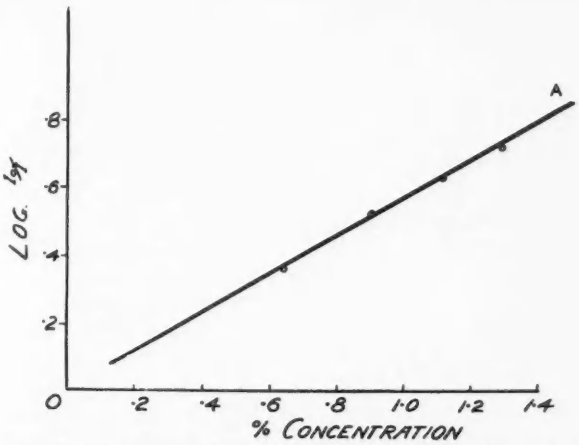

FIG. 2. *Graph showing the linear relation between log I_0/I and concentration.*

using for the purpose the well known Hilger sector photometer (4). Table I shows how the two methods agreed for a sample of pilchard oil. When it was necessary to determine the absorption spectrum over a wider range, a photographic method with a step-sector (5) was used. Fig. 3 shows diagrammatically the arrangement of the apparatus. By means of a sphero-cylindrical lens, light from an iron arc was condensed upon the slit of a quartz spectrograph (Hilger E. 1) in such a way that

TABLE I

VISUAL DETERMINATIONS OF LOG I_0/I COMPARED WITH THOSE OBTAINED WITH SECTOR PHOTOMETER

Concentration, %	Visual method log I_0/I	Sector photometer log I_0/I
0.75	0.34	0.32
1.00	.51	.49
.43	.21	.21
.43	.21	.23

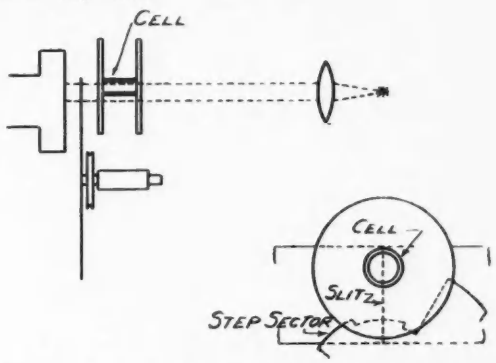

FIG. 3. *The arrangement of the absorption cell and the step-sector.*

the light remained parallel in the vertical plane. The absorption cell was placed close to the slit so that the resulting spectrum was divided into two sections, the light passing through the upper part of the slit being the radiation that had traversed the absorbing solution in the cell, and that incident on the lower part being the comparison beam. The calibration of the comparison beam was effected by means of the step-sector placed between the slit and the cell. The sector was arranged so that both beams were intermittent. The construction of the absorption cell did not eliminate errors due to reflection and absorption at the cell windows. However, these errors would not affect, materially, the shape of the absorption curve, within the wave-length range used in this work. A Moll microphotometer was used for measuring the densities of the plates.

As a solvent, spectroscopically pure cyclohexane was used throughout the experiment. Solutions were prepared and allowed to stand for 12 hr., otherwise different portions of the solution gave different values for k. The quartz windows were cemented with a commercial cement called "liquid solder," which has two advantageous properties. It is not soluble in cyclohexane, and it is easily removed when the cell is dismantled in order to clean it.

Results

Several samples of pilchard oil were studied. Two of these, as listed in Table II, were also tested biologically.* In order to check the method, a biologically tested cod liver oil and a standard solution of Vitamin A† were tested and the results included in Table II.

TABLE II

COMPARISON OF THE BIOLOGICAL AND PHYSICAL DETERMINATIONS OF VITAMIN A CONTENT

Sample	Vitamin A content	
	Biological	Physical
Standard solution	12,500	11,700
Cod liver oil	650	620
Pilchard oil No. 1	120	380
Pilchard oil No. 2	175	580

The second column in the table was obtained by multiplying the extinction coefficient for a 1% solution by a conversion factor of 1600. Somewhat lower values for the conversion factor have been used by some workers but this value gave a very good agreement, between our results and the biological tests, for the standard solution and the cod liver oil. In the case of the pilchard oil there is a very large discrepancy between the results obtained and the biological values. The high values given by the spectroscopic method must be caused by other absorbing substances in the oil. That such extraneous absorption is common in the oils of low Vitamin A potency has been observed by other workers (8). In many cases it has been shown to be due to the free fatty acids which can be eliminated by saponification. A sample

*On albino rats by B. E. Bailey of the Fisheries Experimental Station, Biological Board of Canada, Prince Rupert Station.

†Obtained from British Drug Houses, Ltd., through the courtesy of Charles Anders.

of pilchard oil No. 1 was therefore saponified (1) and its absorption spectrum before and after saponification was obtained by the method previously described. These absorption curves are shown in Fig. 4. The extinction

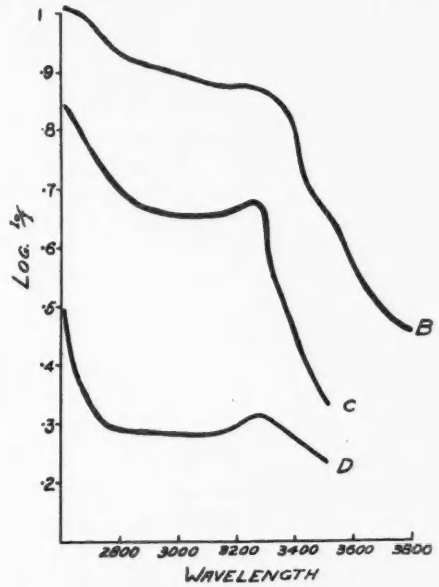

FIG. 4. *Absorption spectra of pilchard oil. Curve B, the normal oil; Curve C, the unsaponifiable fraction of the oil; Curve D, the unsaponifiable fraction of a sample in which the Vitamin A had been previously destroyed by oxidation at 90° C.*

coefficient at 3280Å, as determined from Curve *C*, was somewhat less than that given by Curve *B*, thus showing some absorption by fatty acids in the oil. However, the corrected value of the Vitamin A content, 300, was still too large to compare favorably with the biological assay of 120 units.

There was a further possibility that the pigment in the oil might have an absorption band near 3300Å. This was investigated by finding the extinction coefficient of the oil after decolorizing with diatomaceous earth. It was found that the decrease in k at 3280Å, after decolorizing the oil, was small. Since the action of diatomaceous earth is oxidizing as well as absorptive, it might be expected to remove some of the Vitamin A. The small decrease in absorption observed would indicate that the absorption at 3280Å of the pigment in the oil is negligible.

It was concluded that some other unsaponifiable material was the cause of the remaining discrepancy, and that if the Vitamin A could be eliminated from the oil, its unsaponifiable fraction would show an absorption at 3280Å which would be due to this unknown material. This absorption might then be subtracted from the value obtained in the preceding determination, and

the difference should give a value for the true Vitamin A content. To eliminate the Vitamin A the oil was oxidized for five hours by bubbling air through it at 90° C. The unsaponifiable fraction was then studied spectroscopically. Curve *D* (Fig. 4) was thus obtained. The difference in the extinction coefficient at 3280Å between Curves *C* and *D* is equivalent to 160 units of Vitamin A, which corresponds more favorably with the biological value of 120 units. It may be observed that the absorption decreased not only at 3280Å but also lower down in the ultra-violet. This can be explained if it is assumed that some of the material which had an absorption band in the lower region was destroyed along with the Vitamin A. As its absorption band might extend to 3280Å the difference in the extinction coefficient at this wave-length between Curves *C* and *D* may not be due entirely to Vitamin A. The value of 160 units, therefore, obtained from this procedure is subject to a correction which can be ascertained only by treating the oil in such a way that the Vitamin A alone would be destroyed. Any method by which the Vitamin A could be removed from the oil without otherwise modifying it would provide a more accurate means of checking the results obtained by any spectroscopic method of analysis.

Acknowledgments

The authors take pleasure in acknowledging the co-operation and assistance given by Dr. Neal M. Carter and Mr. Basil E. Bailey of the Fisheries Experimental Station (Biological Board of Canada), Prince Rupert, B.C.

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VIBRATIONS OF POWER LINES IN A STEADY WIND

II. SUPPRESSION OF VIBRATIONS BY TUNED DAMPERS[1]

By R. Ruedy[2]

Abstract

Vibration of power lines is prevented by attaching in each span, at a distance b from the end, one or two dampers which consist in principle of a heavy mass M fastened to the end of a spring (Holst damper), or to both ends of a thin cantilever suspended at its centre, or to a cable (Stockbridge damper). The mathematical study of the forces in a span provided with a damper and subjected to a tension T furnishes the constants necessary for the proper designing of dampers. For an incoming angular frequency p, the ratio, undamped to damped amplitude, is in practice equal to $1 - p^2bMD/T$, where D is the ratio of the force exerted by a spring upon a solid support to the force applied to its mass. Dampers suspended at the end of the first quarter of the loop length and tuned to the frequency at which the conductor vibrates, suppress, from a practical standpoint, the motion of the entire span when their damping factor amounts to a few units and their weight is equal to the weight of a loop length of conductor. By choosing different frequencies for the dampers used on a given span, and by taking advantage of the coupling existing between them, a fairly wide band of frequencies may be suppressed.

Vibration and Fatigue Failures

In careful design the conductor in the spans of a power line is so strung that during the times of severest loads, which are to be expected at minimum temperature and with the worst ice coatings and the highest winds, the tension in the cable will not exceed a value of about 75 to 100% of the elastic limit of the metal in question. But the proportional limit and the breaking point refer to more or less immediate effects produced by the load. Indeed, when different loads are left suspended on rods or wires of the same size, a smaller load may cause a wire to break, providing that it be allowed to act for a longer time.

Like conditions prevail with respect to alternating forces. The endurance limit is defined as that stress per unit area that may be applied to a given material for an indefinitely large number of cycles without producing rupture, supposing, of course, that such a limit exists. The endurance limit is found by counting the number of cycles of pulling, bending or twisting that a sample stands without becoming damaged under different reversing forces, and by plotting the critical stress S, or its logarithm, as a function of the logarithm of N, the number of cycles. Plotting against the number of cycles is unreliable (6). For all wrought ferrous metals and for a certain number of light metals, such as rolled aluminium and extruded magnesium, the *S versus* log N graph for flexure shows a sharp bend as the load is reduced, and changes to the horizontal direction at less than 10 million cycles. For rolled aluminium the critical stress is given as 11,000 lb. per sq. in. in reversed flexure; the average tensile strength is about 30,000 lb. per sq. in. There is a second class of materials for which the curve representing the limiting stress as a function

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Contribution from the Division of Research Information, National Research Laboratories, Ottawa, Canada.

[2] *Research Investigator, National Research Laboratories, Ottawa.*

of log N keeps falling even beyond the sharp bend of the curve. This behavior is shown by cold drawn copper, and to a slighter degree by annealed copper, but an endurance limit of about 10,000 lb. per sq. in. may somewhat arbitrarily be chosen (6). The tensile strength of hard drawn copper is 58,000 to 68,000 lb. per sq. in. For hot rolled unannealed Monel metal and duralumin the endurance limit is inversely proportional to the logarithm of the number of cycles throughout the entire range tested, up to at least 1000 million cycles. When a "wind" of 50 cm. per sec. blows against a power line of 1 cm. diameter, the eddy frequency $f = 0.2U/d$ is 10 cycles per sec. As a frequency of only one cycle per second corresponds to 86,400 cycles per day, an average of 100 days of continued feeble wind in the first year brings the number of vibrations which a newly strung conductor makes, well into the range of cycles for which the endurance limit, and not merely the tensile strength, has to be taken into account in designing the line. Failures appear in the form of fractures more or less perpendicular to the axis of the wire, with no sign of yielding as in ordinary overstressed pieces. Their number increases rapidly with time; if s failures are observed in the first year, as many as 2^3s failures occur after two years (1). The highest stresses are likely to be found near the clamps by which the wires are fastened, unless the core of the cable is made to act as a support for the conducting shell. Slight scratches, or hidden cracks and faults, aggravate the effects of fatigue.

In view of the uncertainty of the endurance limit, particularly in materials not always handled with the utmost care and exposed to corrosion and scratching, the safest method of prolonging the life of conductors seems to be to suppress vibrations as completely as possible, either by removing the causes or by rendering displacement more difficult.

Direct Methods of Suppressing Vibrations

The formation of eddies is prevented in struts used on aeroplanes by giving them drop-shaped or streamlined contours, but if this change were made in the case of transmission lines the greater curvature then obtained in certain portions of the cross-section would increase corona losses. A slight flattening should, however, overcome some of the difficulties and increase the damping. The only other remedy to prevent the formation of eddies is to shield the line from the wind: in hilly or wooded country vibrations give little trouble. In some exposed regions it will also be possible to have the power lines run along, and not across, the direction of the most frequent winds.

When it is not possible to prevent the formation of eddies, forces may be applied which directly oppose the impulses given by the eddies to the wire. The only force that lends itself readily to this end along the entire span is the horizontal component of the magnetic field of the earth, about 1/5 gauss. But even with currents of 100 to 200 amp. flowing in wires 2 to 3 cm. thick, the forces exerted by the magnetic field are but a few dynes per centimetre, or several times less than the forces that a low wind would produce, so that, quite apart from the difference in the frequency, this method does not offer an effective remedy.

It is not, however, necessary, in order to keep mechanical vibrations within bounds, to apply opposing forces along the entire length of the span. A periodic force $Q \cos pt$ acting at the single point $\sigma = b$ (or at the symmetrical point $\sigma = s - b$ near the other end of a string of length s) produces the same effect as a force $mP \cos ptd\sigma$ acting in opposite phase upon each element of mass $md\sigma$ of the string, provided that the initial conditions, such as, for instance, the shape of the conductor, etc., be the same, and that, in addition (7, p. 187),

$$Q_b = \frac{msP}{\sin(\kappa\pi b/s)},$$

where κ is the number of loops. This equation, which is useful when an effort is made to reproduce by machine or by hand the vibrations caused by the wind, shows that the force required is small when it is applied in the centre of the loop where $b = l/2\kappa$. At a node, where $b = s/\kappa$ or a multiple of s/κ, even the most intense force is without effect. In any case the amplitudes become large only when the frequency of the applied force coincides with one of the resonance frequencies $\kappa(T/m)^{\frac{1}{2}}/s$ of the span, which is under a tension T.

The Tuned Spring Damper

While a system of relays controlled by the vibrating cable, the current and the wind could be used in serious cases to generate and apply the required opposing forces, it is simpler to let the point of application itself create the opposing force by attaching to it a spring carrying a weight, which is forced to move through a viscous fluid held in a vessel fastened to the string. The displacement of the suspension point stretches and compresses the spring in turn and creates an alternating force K that opposes the displacement in the rhythm of the vibration. Devices of this kind are variously called dynamic dampers, or absorbers, or resonance dampers with viscous damping. They act by a combination of the inertia of their mass, the elastic force and the resistance due to friction, and even when no wind is blowing and the conductor hangs quietly, the shape of the equilibrium curve is altered. In order to study the action of the spring damper it is therefore necessary to find for the vibration of the string, a solution that can be adapted to the changed initial shape created by the presence of the spring damper (Fig. 1).

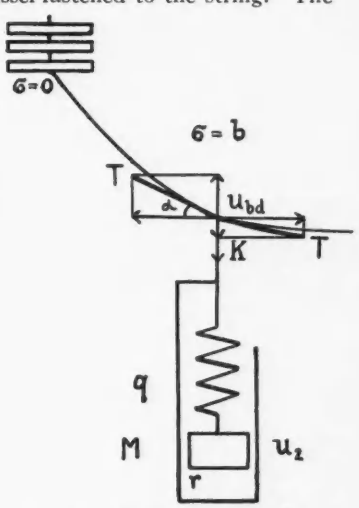

FIG. 1. *Effect of spring damper on flexible string, on the assumption that the horizontal tension is only slightly changed.*

On the assumption that the displacement u of the string varies as ϵ^{ipt}, or a sum of such terms, and in the absence of an external force ($P = 0$), the equation

$$\frac{\partial^2 u}{\partial t^2} + 2k\frac{\partial u}{\partial t} - c^2\frac{\partial^2 u}{\partial \sigma^2} = mP\epsilon^{ipt},$$

which applies to the string on either side of the damper, can be written (7, p. 192)

$$\frac{\partial^2 u}{\partial \sigma^2} + \frac{1}{c^2}(p^2 - 2ikp) = 0,$$

which has for its general solution, with

$$\lambda^2 = (p^2 - 2ikp)/c^2,$$
$$u = (C_1 \sin \lambda\sigma + C_2 \cos \lambda\sigma)\epsilon^{ipt},$$

or a sum of such terms. The damping factor k depends in practice on the frequency. On the other hand, a particular solution of the complete equation is found in the form

$$u = C_3 \sin pt \sin \kappa\pi\sigma/s.$$

As a general solution the combination

$$u = (C_1 \sin \lambda\sigma + C_2 \cos \lambda\sigma + C_3 \sin \kappa\pi\sigma/s)\epsilon^{i(pt+\epsilon)}$$

may as usual be tried. The left-hand portion of the span between the pole and the point at which the spring is attached will have to satisfy the condition that the displacement $u = 0$ at $\sigma = 0$ (at the insulator) and $u = u_b$ at $\sigma = b$. This is the case if

$$u_L = (u_b - C_3 \sin \kappa\pi b/s)\frac{\sin \lambda\sigma}{\sin \lambda b} + C_3 \sin \kappa\pi\frac{\sigma}{s},$$

omitting the time function ϵ^{ipt}, since only the local amplitudes are of importance.

Similarly, for the right-hand portion of the span, $u = u_b$ for $\sigma = b$, and $u = 0$ for $\sigma = s$. This gives

$$u_R = \left(u_b - C_3 \sin \kappa\pi\frac{b}{s}\right)\frac{\sin \lambda(s - \sigma)}{\sin \lambda(s - b)} + C_3 \sin \kappa\pi\frac{\sigma}{s}.$$

At the point b, where the two sections meet, there is a slight kink in the cable owing to the weight of the mass attached to the spring, and the two equations give a different tangent. The tension thus created in the string is equal to

$$K = T\left(\frac{\partial u_L}{\partial \sigma} - \frac{\partial u_R}{\partial \sigma}\right)_{\sigma = b}$$

$$K = T\lambda\left(u_b - C_3 \sin \kappa\pi\frac{b}{s}\right)\left(\frac{\cos \lambda(s - b)}{\sin \lambda(s - b)} + \frac{\cos \lambda b}{\sin \lambda b}\right)$$

or

$$T\lambda\left(u_b - C_3 \sin \kappa\pi\frac{b}{s}\right)\frac{\sin \lambda s}{\sin \lambda b \sin \lambda(s - b)}$$

that is,

$$u_b = \frac{K}{\lambda T}\frac{\sin \lambda b}{\sin \lambda s}\sin \lambda(s - b) + \frac{C_3}{\lambda\Gamma}\sin \kappa\pi\frac{b}{s}, \text{ or a sum of such terms.}$$

In the steady state this force must be equal to that created in the spring. Taking the most general case, where a mass M attached to the spring is supposed to move in a viscous fluid contained in a cylinder carried by the wire, the force of friction being proportional to the relative velocity between string and spring weight, if (Fig. 1)

q = the spring constant, or the restoring force for 1 cm. relative displacement of the spring weight,

M = the mass suspended from the conductor, including if necessary one-third of the mass of the spring (10, p. 55),

τ = the period of the vertical oscillation of M regardless of friction,

$N = \sqrt{q/M}$ = the angular velocity at resonance, equal to $2\pi/\tau$, without damping,

$d = R/2M$ = the coefficient of damping of the spring system,

$c = \sqrt{T/m}$ = the wave velocity for transverse waves along the string,

and, if, in addition, u_2 is the displacement of the mass M of the damper from its position at rest, then (2, p. 61),

$$K = (u_2 - u_b)(q + iRp) ,$$

while, with respect to the acceleration of M,

$$(u_2 - u_b)(q + iRp) = u_2 Mp^2 ,$$

so that

$$u_2 = u_b \frac{q + iRp}{q + iRp - Mp^2}$$

and

$$K = u_b Mp^2 \frac{N^2 + i2pd}{N^2 + i2pd - p^2} .$$

From the two expressions for K, an equation for u_b may be derived:

$$u_b = \frac{C_3 \sin \kappa\pi \frac{b}{s}}{1 - \frac{Mp^2}{T} \frac{N^2 + 2ipd}{N^2 + 2ipd - p^2} \frac{\sin \lambda b \sin \lambda s\left(1 - \frac{b}{s}\right)}{\lambda \sin \lambda s}} .$$

By introducing this value in the equation for the left- or right-hand portion of the span, the motion of the string as influenced by the damper can be followed from point to point. It is usual, however, to suspend a damper near both ends of the span. The equation for the left-hand portion then remains the same:

$$u = \frac{u_b - C_3 \sin \kappa\pi \frac{b}{s}}{\sin \lambda b} \sin \lambda\sigma + C_3 \sin \kappa\pi \frac{\sigma}{s} ,$$

whereas for the middle portion the condition that $u(\sigma) = u(-\sigma)$ and $u = u_b$ for $\sigma = b$ arises. In this case κ must be an even number and

$$u_m = \frac{u_b - C_3 \sin \kappa\pi \frac{b}{s}}{\sin \lambda(s - 2b)} \left(\frac{\sin \lambda s/2}{\cos \lambda s/2} \sin \lambda\sigma + \cos \lambda\sigma \left(\sin \lambda(s - b) - \sin \lambda b\right)\right) + C_3 \sin \kappa\pi \frac{\sigma}{s} .$$

The difference between the tangents to the left and right of $\sigma = b$ becomes

$$\Delta = \lambda\left(u_b - C_3 \sin\frac{\kappa\pi}{l}b\right)\frac{\cos\lambda s/2}{\sin\lambda b\cos\lambda(b - s/2)},$$

and finally

$$u_{bd} = \frac{C_3 \sin\kappa\pi\frac{b}{s}}{1 - \frac{M}{T}\frac{p^2}{\lambda}\frac{N^2 + 2ipd}{N^2 + 2ipd - p^2}\sin\lambda b\frac{\cos\lambda s\left(\frac{1}{2} - \frac{b}{s}\right)}{\cos\lambda s/2}}$$

for two dampers symmetrically placed near the ends of the span. The ratio between u_b, the undamped amplitude (for $M = 0$), and u_{bd}, the artificially damped amplitude, is, since $mc^2 = T$,

$$\frac{u_b}{u_{bd}} = 1 - \frac{M}{m}\frac{p^2}{c^2}\frac{N^2 + 2ipd}{N^2 + 2ipd - p^2}\frac{\sin\lambda b}{\lambda}\frac{\cos\lambda s\left(\frac{1}{2} - \frac{b}{s}\right)}{\cos\lambda s/2},$$

and should be made as large as possible. The result differs from known formulas (5) in that it takes friction into consideration.

Since b/s is much less than $1/2$, the ratio becomes

$$\frac{u_b}{u_{bd}} = 1 - \frac{M}{T}p^2\frac{\sin\lambda b}{\lambda}\frac{N^2 + 2ipd}{N^2 + 2ipd - p^2},$$

regardless of whether one or two dampers symmetrically placed be used. The second damper serves to suppress the even numbered overtones.

Below critical damping, $k = p$, of the string, the fraction k/p is less than unity so that

$$\lambda = \sqrt{\frac{p^2}{c^2} - i2k\frac{p}{c^2}} \doteq \frac{p}{c} - i\frac{k}{c},$$

and

$$\sin\left(\frac{p}{c} - i\frac{k}{c}\right) = \sin\frac{p}{c}\cosh\frac{k}{c} - i\cos\frac{p}{c}\sinh\frac{k}{c};$$

the absolute value of $\sin\lambda b$ is, therefore,

$$\left|\sin\left(\frac{p}{c} - i\frac{k}{c}\right)b\right| = \sqrt{\sinh^2 k\frac{b}{c} + \sin^2 p\frac{b}{c}} = \sqrt{\frac{\cosh 2k\frac{b}{c} - \cos 2p\frac{b}{c}}{2}}.$$

The absolute value of $u_b/u_{bd} - 1$ becomes

$$\left|\frac{u_b}{u_{bd}} - 1\right| = -\frac{M}{m}\frac{p}{c}\sqrt{\frac{\cosh 2\frac{k}{p}\frac{p}{c}b - \cos 2\frac{p}{c}b}{2\left(1 + \frac{k^2}{p^2}\right)}}\sqrt{\frac{1 + \frac{4d^2}{N^2}\frac{p^2}{N^2}}{\left(1 - \frac{p^2}{N^2}\right)^2 + \frac{4d^2}{N^2}\frac{p^2}{N^2}}},$$

so that the influence of the string constants and that of the spring constants appear as separate factors, and may together with M/m be so adjusted that the ratio $(u_b - u_{bd})/u_{bd}$ exceeds, say 10; in this case u_b is reduced to about 9% of its former value.

Discussion of Results

It is necessary first to discuss briefly the four factors entering into the equation for $(u_b - u_{bd})/u_{bd}$.

The factor p/c increases steadily as the frequency $p/2\pi$ of the external force increases. Since, for progressive waves, the relation $p/c = 2\pi/\lambda$ holds, the ratio mc/p may be considered as $1/2\pi$ times the mass of a length of string equal to the wave-length corresponding to the frequency impressed upon the string.

The other factor referring to the constants of the conductor span, namely the difference between the hyperbolic cosine of $2kb/c$ and the ordinary cosine of $2pb/c$, is always a positive number. It is small for low frequencies, that is, small values of p/c. The largest values are obtained when b is so chosen that the ordinary cosine vanishes, that is, when $b = \lambda/8$. The distance b should therefore be shorter than half the length of the loop corresponding to the highest frequency $p = 2\pi c/\lambda$ to be expected for the most frequent wind speed.

The ratio k/p may be considered as approximately constant for a given conductor, and inversely proportional to the radius, while in reality, though only for very slow motions, it is proportional to the square root of the frequency. At the same time the value of k must be smaller than that for critical damping, $k_c = 2\kappa\pi c/s$.

The last factor in the reduction formula depends upon the frequency to which the spring damper is tuned, and, as is known from vibration engineering practice, represents the fraction of an alternating force, in the present case $u_b M p^2 \epsilon^{ipt}$, that is transmitted over a spring damper to a solid support, or from a vibrating support to the mass attached to a spring, that is, it measures the ratio, transmitted force to impressed force, or the transmissibility, D_2. When for a given coefficient of damping the impressed frequency is very low, compared to the natural frequency of the spring damper ($p < N$), the mass M completely follows the motion of the string as if it were rigidly tied to the string, and the factor becomes equal to unity. At resonance ($N = p$) the factor is equal to $(1 + p^2/4d^2)^{1/2}$ and, except when $d > N$, is therefore greater than unity. For very large values of p, on the other hand, the mass M of the damper is unable to follow the motion of the string; it remains at rest and the transmissibility is reduced to zero. While resonance is undesirable when the problem is to prevent vibrations from spreading, it is essential for reducing the vibrations of a string by means of a spring damper, and a natural frequency of the damper smaller than $1/\sqrt{2}$ times the string frequency should not be chosen. When the damper is tuned to the external frequency, the transmissibility reaches very high values so long as the damping coefficient d is small. When the damping increases to very large values, the damper is virtually prevented from moving relatively to the string, so that again it acts merely as a mass clamped to the string. While lessening the damping increases the effect upon the string, a certain amount of damping is nevertheless necessary, because the value of

$$u_2 = u_b D_2 ,$$

has to be kept within safe limits. Another reason for introducing damping is that in the case of the power line the damper should reduce the amplitude over a certain range of frequencies.

For each choice of d there is a frequency at which D_2 reaches its highest value. When d is a certain fraction, η, of N and $\nu = p/N$, the factor D_2 is given by

$$D_2^2 = \frac{1 + 4\eta^2\nu^2}{(1 - \nu^2)^2 + 4\eta^2\nu^2} .$$

This expression reaches a maximum for a given value of η when

$$2\eta^2\nu^4 + \nu^2 - 1 = 0 .$$

Provided that the damping is so small that the first term may be neglected, the maximum is obtained at resonance ($\nu = p/N = 1$). When the damping is appreciable, the peak lies at

$$\nu^2 = \frac{-1}{4\eta^2} \pm \frac{1}{4}\sqrt{\frac{8}{\eta^2} + \frac{1}{\eta^4}} .$$

The peak is high but narrow when friction in the damper is small; it is low and broad when there is much damping, so that the choice of the value of $2d$ depends on the range of frequencies to be suppressed. The better damping obtained for small values of $2d$ is moreover accompanied by large excursions, u_2, of the mass M of the damper which are likely to overtax the endurance of the spring.

For small values of kb/c and pb/c, the following formula holds:

$$\cosh 2kb/c - \cos 2pb/c = 2\frac{k^2b^2}{c^2} + 2\frac{p^2b^2}{c^2} = 2\frac{b^2}{c^2}p^2\left(1 + \frac{k^2}{p^2}\right) ,$$

so that

$$\left|\frac{u_b}{u_{bd}} - 1\right| = -\frac{M}{m}\frac{p^2b}{c^2}\sqrt{\frac{1 + \frac{4d^2}{N^2}\frac{p^2}{N^2}}{\left(1 - \frac{p^2}{N^2}\right)^2 + \frac{4d^2}{N^2}\frac{p^2}{N^2}}} = -\frac{M}{T}bp^2\sqrt{\frac{1 + 4\eta^2\nu^2}{(1 - \nu^2)^2 + 4\eta^2\nu^2}} ,$$

and it seems safe to use this formula, which does not depend on the damping of the string, in most practical cases.

The following example illustrates the relative influence of the various factors. A damper is to be designed for a stranded aluminium conductor of No. 00 B. & S. gauge (0.414 in. diameter, or about 1.2 cm.) suspended between two fixed points at the same elevation, 160 metres (480 ft.) apart and so strung that the maximum stress does not exceed 14,000 lb. per sq. in. with a combined load of 0.5 in. ice coating and a 47-mile-an-hour wind (5 lb. pressure per sq. ft.) at $-20°$ F. The sag without this load at the centre of the span is then 16.5 ft. at $-14°$ F., 18 ft. at 34° F. and 19.7 ft. at 90° F., the total tension varying between about 220 and 183 lb. (9, p. 123). The weight per foot of conductor is 0.125 lb.; therefore c is about 210 ft. per sec. (or 6280 cm. per sec.) at the highest temperature. If the average wind velocity is from three to four miles per hour, frequencies of about 30 cycles per second will be strongly excited; their wave-length is about seven feet ($\lambda/8 = 26$ cm.). The fundamental frequency of the span is about one-half cycle per second.

The influence of the factors p/c, $\sin \lambda/\lambda$ and of the damper D_2 (for which $2d$ has been assumed to be equal to 10, while $N_2 = 25$, making the damping critical for $d = 25$) may be seen from Table I. By computing the value of

TABLE I

EFFECT OF TUNED DAMPER ON VIBRATING STRING

($c = 2000\pi$ cm. per sec.)

Resonance frequency, 25 cycles per sec., $d/d_{cr} = 0.032$

f	$2\pi f = p$	p/c	D_2		$b = 10$ cm.		$b = 20$ cm.	
			$2d_2 = 50$	$2d_2 = 10$	$\frac{c}{p}\frac{\sin\lambda}{\lambda}$	$\left(\frac{u_b}{u_{bd}}-1\right)\frac{m}{M}$	$\frac{c}{p}\frac{\sin\lambda}{\lambda}$	$\left(\frac{u_b}{u_{bd}}-1\right)\frac{m}{M}$
0.5	π	0.0005	1.00	1.00	0.005	0.000	0.01	0.000
1	2π	0.001	1.00	1.00	0.010	0.000	0.02	0.000
5	10π	0.005	1.01	1.00	0.05	0.000	0.10	0.0005
10	20π	0.010	1.16	1.19	0.10	0.001	0.20	0.002
15	30π	0.015	1.25	1.65	0.15	0.004	0.30	0.007
20	40π	0.020	1.45	2.57	0.20	0.010	0.39	0.020
21	42π	0.021	1.49	2.85	0.21	0.012	0.41	0.025
22	44π	0.022	1.47	3.05	0.22	0.015	0.43	0.029
23	46π	0.023	1.47	4.23	0.23	0.022	0.44	0.043
24	48π	0.024	1.43	4.86	0.24	0.028	0.46	0.054
25	50π	0.025	1.41	5.00	0.25	0.031	0.48	0.060
26	52π	0.026	1.38	4.52	0.26	0.030	0.50	0.059
27	54π	0.027	1.35	3.80	0.27	0.028	0.51	0.052
28	56π	0.028	1.32	3.16	0.28	0.025	0.53	0.048
29	58π	0.029	1.26	2.39	0.29	0.020	0.55	0.038
30	60π	0.030	1.18	1.87	0.30	0.017	0.57	0.033
35	70π	0.035	1.02	2.90	0.34	0.011	0.64	0.021
40	80π	0.040	0.7	0.56	0.39	0.009	0.72	0.016

Damping is satisfactory over a band of about five cycles on each side of the resonance frequency N_2.

$\sin \lambda/\lambda$ for two distinct values of natural damping of the cable, namely 0 and 0.25 for the resonance frequency, varying as the square root of the frequency, it is shown that within these limits natural damping produces relatively little effect, and the final results refers to the absence of friction. The contribution of the damper for $M/m = 1$ is several times larger, but the value of c in p/c is responsible for a low total reduction. In order to bring the amplitude down to about 10% of the original displacement at $\sigma = b$, it is therefore necessary to give M/m a value of several hundred units, that is, to make the mass of the damper equal to the mass of a length of cable about equal to the wave-length of the frequency to be damped ($\lambda = 2\pi c/p$). Dampers of this kind have been found in many tests to completely suppress the vibrations of the cable (5).

As a second example, a 500,000 circular-mil stranded copper cable (diameter 0.813 in., weight 1.54 lb. per ft.) may be discussed. The elastic limit is 28,350 lb. per sq. in.; the maximum allowable tension, 75% of the elastic limit, is about 8350 lb. when the ice is 0.5 in. thick (0.8 lb. per ft.); and the wind

pressure 10 lb. per sq. ft. (wind load 1.5 lb. per ft.). As the tower spacing is varied from 300 to 1200 ft.(90 to 360 metres), the permissible tension without wind and ice varies between 3620 lb. at 100° F. and 6800 lb. at −10° F. for the 300 ft. span, and between 4500 lb. (at 100° F.) and 4750 lb. (at −10 °F.) for the 1200 ft. span (9, p. 205). The velocity of propagation, c, for the 1200 ft. span is therefore between 310 and 320 ft. per sec. or at the most 3000π cm. per sec., while for the 300-ft. span it varies between 1275 ft. per sec. (8250 cm. per sec.) at the highest temperature and nearly 363 ft. per sec. (10,890 or 3500π cm. per sec.) at the lowest temperature (3, p. 205).

The main change with respect to the first example is the change of the wave velocity from 2000π to 3000π cm. per sec., resulting in shorter loops for standing waves of the same frequency, while, on account of the doubled diameter, winds of the same speed now produce correspondingly lower frequencies. The value of p/c is reduced by about one-third, the value of the factor $\sin \lambda/\lambda \div pb/c$ is reduced in that k is smaller for larger diameters, while b, on account of the larger value of c, will have to be increased so that it may offset the change in p/c. The damper has to be tuned to 12.5 cycles per second in place of the former value of 25 cycles. If the same damper were used it would produce only about one-third or one-fourth as much effect as it would on the line for which it had been designed.

Application of the Theory of Damping

While given for a definite form of damper used to some extent on power lines (4, 5), namely, a spring with a heavy mass attached to one end and viscous damping proportional to the velocity of the mass with respect to the support, the theory is readily adapted to various simpler types of actual or possible dampers. It is merely necessary to insert the proper value for the force K exerted at the suspension point. In the tuned damper itself the spring may be replaced by a piece of rubber with high internal friction.

When frictional forces proportional to the velocity of the mass of the damper are used, as in air damping or electric damping,

$$K = u_2 M p^2 = iu_2 Rp + (u_2 - u_b)(q + iRp)$$

or

$$K = u_b M p^2 \frac{N^2}{N^2 + i2pd - p^2}$$

so that the only change with respect to the damper discussed before, in which friction is proportional to the relative velocity between damper and string, is the suppression of the term $i2pd$ in the numerator of D_2. With the amount of damping used in practice the difference is slight.

Vibrating rods or blades attached to the conductor with or without masses fastened to them are thus but a special form of the spring damper. In the simplest case a steel blade l cm. long, w cm. wide and h cm. thick may be clamped with one end at some point along the span, and a mass M fastened to the other end of the blade (Fig. 2-I). When the vibrations are so small

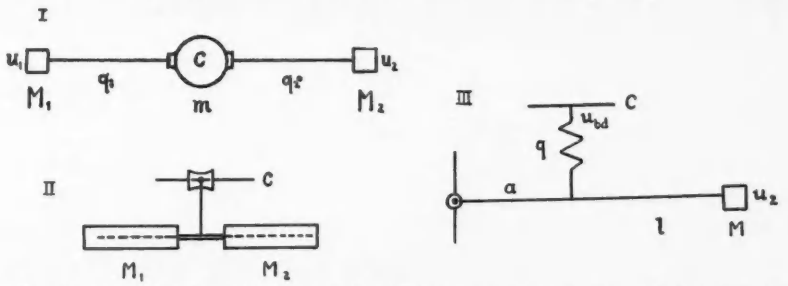

FIG. 2. *Various devices based on the principle of the tuned spring damper. In I, thin cantilevers serve for tuning in place of springs. II is the widely used Stockbridge damper, the over-all length being about 50 cm. and M_1 and M_2 each weighing 3 to 4 kg.*

that the mass moves sensibly up and down only, a force P at the free end of the cantilever gives a deflection $u_2 = Pl^3/3EI$, where E is Young's modulus of elasticity and I the moment of inertia of the cantilever, namely, $bh^3/12$ for vibrations taking place in the stiffer cross-section and $bh^3/48$ for vibrations taking place in the more flexible cross-section. The spring constant is therefore

$$q = P/u_2 = 3EI/l^3 .$$

When the loaded blade is replaced by a cylindrical bar or cable (4, 8), as is the case in the Stockbridge damper, $I = \pi d^4/64$. Apart from the different meaning of the elastic constant, the theory of this damper (Fig. 2-II) is the same as that of the tuned spring damper. At the limit the damper becomes simply a rod or strip of metal of length of about one loop attached to the cable and vibrating in its natural frequencies (4, 8).

In some cases it may be possible to fasten one end of the cantilever to a pin on the mast, and to let the mass act with the lever arm l on the spring suspension (Fig. 2-III). The effective spring constant is changed to aq/l.

Broadening of Resonance Through Coupling

By choosing dampers tuned to the different frequencies, damping is obtained over a wider range of frequencies. A broadening of the response of the damper is also due to the fact that the vibrating mass of the conductor effects a coupling between the dampers, whether these are used side by side or are symmetrically placed near the two ends (Fig. 2-I). If m_3 designates a vibrating mass representing the string, m_1 and m_2 and q_1 and q_2 the mass and spring constants of the dampers, and u_1, u_2 and u_3 the displacements, the equations

$$\begin{aligned} m_1\ddot{u}_1 + k_1(u_1 - u_2) &= 0 \\ m_2\ddot{u}_2 + k_1(u_3 - u_2) &= 0 \\ m_3\ddot{u}_3 + k_1(u_1 - u_3) + k_2(u_3 - u_2) &= 0 , \end{aligned}$$

hold for longitudinal or small transverse motions, and the angular resonance frequencies are given by

$$N^4 - N^2\left(k_1\frac{(m_1 + m_3)}{m_1m_3} + k_2\left(\frac{m_2 + m_3}{m_2m_3}\right)\right) + \frac{m_1 + m_2 + m_3}{m_1m_2m_3} = 0 .$$

When m_3 is larger than either m_1 or m_2, the two solutions are

$$N^2 = \tfrac{1}{2}\left(\frac{k_1}{m_1} + \frac{k_2}{m_2}\right) \pm \sqrt{\tfrac{1}{4}\left(\frac{k_1}{m_1} - \frac{k_2}{m_2}\right)^2 + \frac{m_1 m_2}{m_3^2}\,\frac{k_1}{m_1}\,\frac{k_2}{m_2}}.$$

or, writing N_1 for k_1/m_1 and N_2 for k_2/m_2

$$N^2 = \tfrac{1}{2}(N_1 + N_2) \pm \sqrt{\tfrac{1}{4}(N_1 - N_2)^2 + \frac{m_1 m_2}{m_3^2} N_1 N_2}.$$

Coupling of the dampers through the conductor, therefore, lowers the frequency of the damper with the lower frequency, and increases the frequency of the damper tuned to the higher frequency. If the two frequencies are not too far apart, the entire band between them is reduced in amplitude.

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THE SUBSTITUTION OF METHYLENE BLUE THIOCYANATE FOR METHYLENE BLUE CHLORIDE IN THE REDUCTION TEST OF MILK[1]

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Abstract

Methylene blue thiocyanate has been found to be superior to methylene blue chloride in the reduction test for bacteriological quality of milk, because the thiocyanate is easily prepared in a state of purity approaching 100%.

The widespread use of the methylene blue reduction test on this continent necessitates the frequent duplication of the standard methylene blue chloride tablets certified for this test by the Commission on Standardization of Biological Stains. The reproducibility of a dye involves purification or at least determination of purity. The difficulties encountered in such procedures in the case of methylene blue chloride are serious (1).

At the request of the chairman of the Commission on Standardization of Biological Stains, the authors undertook the present investigation in an attempt to develop improved standards for the methylene blue reduction test. Since it crystallizes readily from aqueous solution without water of crystallization, methylene blue thiocyanate seemed to offer possibilities as a substitute for methylene blue chloride in this test.

Preparation and Analysis of Methylene Blue Thiocyanate

The exhaustive and excellent work of Clark, Cohen and Gibbs (1) has shown that methylene blue chloride is difficult to purify. Various samples prepared by these workers contained excess chlorine and excess sulphur, and gave evidence of small percentages of electromotively active impurities. Drying was found to destroy progressively the characteristic properties. They even suspected slight denaturation when desiccation was carried out at low temperatures.

The work of Drew and Head (4) indicates that methylene blue thiocyanate might have some properties superior to those of the chloride. They report that "Methylene-blue thiocyanate was obtained from the chloride and KCNS in lustrous needles which occurred in two forms: (1) golden-brown (Found:

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C, 59.0, 59.0; H, 5.35, 5.35. $C_{17}H_{18}N_4S_2$ requires C, 59.6; H, 5.25%); (2) beetle-green (Found: C, 58.95; H, 5.3%). The two forms separated from the same mother-liquor." One important fact is that it crystallizes from aqueous solution readily, apparently with *no water* of crystallization or water of constitution. Such is not the case with the methylene blue chloride, some of the purest samples of which are only 89% pure with respect to total dye content. Because of this the thiocyanate seemed to offer possibilities as a substitute for methylene blue chloride in the methylene blue reduction test.

In order to obtain some idea regarding the nature of thiocyanates made from different samples of methylene blue chloride obtained from various manufacturers, a series of thiocyanates was prepared. The thiocyanate in every case was prepared from a hot aqueous, nearly saturated solution of the chloride, which was then filtered while still hot. To the hot filtrate was added a slight excess of pure potassium thiocyanate. On cooling, beautiful crystals of the methylene blue thiocyanate separated. They were filtered by suction, washed thoroughly with cold water, and air dried at 50° C. In a few cases crystallization from hot water was carried out three or more times. A sufficient number of data have not yet been accumulated to indicate the extent of purification that can be accomplished by repeated crystallization.

Analysis of the various products was carried out by means of a titanous chloride titration, which gave the total dye content. The titanous salt solution was made from the 15% aqueous solution and diluted to approximately 0.05 *N*. It was stored in an apparatus similar to that of Thornton and Chapman (8) and preserved under hydrogen. It was standardized twice daily against *pure* ferrous ammonium sulphate, which had been oxidized by *N*/50 potassium permanganate. The actual titration was carried out in a 250 cc. Erlenmeyer flask fitted with a three-hole rubber stopper. One hole was for the tip of the burette and the remaining two were for the entrance and exit of nitrogen gas, which was passed through the solution during the titration. The nitrogen used was tank nitrogen supplied by the Ohio Chemical Company. It was thoroughly freed from oxygen by passing it through alkaline pyrogallate and then through 50 cm. of reduced copper gauze contained in a Pyrex tube which was heated electrically.

Table I gives some of the data obtained by the foregoing analytical procedure. The results are the average of two or more closely agreeing determinations.

TABLE I

COMPARATIVE TOTAL DYE CONTENTS OF SAMPLES OF METHYLENE BLUE CHLORIDE AND METHYLENE BLUE THIOCYANATE

Sample	1	2	3	4	5	6	7
Total dye content							
as the chloride, %	87	87.2	80.3	79.9	85.5	59.3	87.5
as the thiocyanate, %	99.7	101.3	101.1	100.6	100.1	99.5	99.8

An inspection of this table indicates the feasibility of converting a chloride of low dye content to a thiocyanate of virtually 100% total dye content.

It must be noted here that an analysis such as that described will not necessarily indicate the presence of small quantities of undermethylated products. For that reason the absorption curves of some of the methylene blue thiocyanates were determined by the Hilger-Nutting spectrophotometer. Undermethylated products can be determined readily with this instrument.

The measurements were made with a standard Hilger wave-length spectrometer provided with a Nutting photometer. The light source was a d.-c. Pointolite lamp. The solutions of methylene blue thiocyanate used were made by diluting an aqueous 0.02% solution 40 times with water. The concentration of the solution is important, since Holmes (5) has shown that in the case of a dye such as methylene blue chloride, the absorption changes with the concentration. Readings were taken using a 2 cm. layer.

Conn (3, p. 64) gives the absorption maximum of methylene blue chloride, if pure, as about 667. Holmes and Peterson (6) have shown definitely that absorption ratios* will enable the analyst to identify dyes conveniently and afford information respecting their purity. These workers show that for methylene blue chloride the absorption ratio is 0.59. It would be expected that in the case of the thiocyanate the absorption curve, the maximum and the absorption ratio would be similar to, if not identical with, those of the chloride. Such is the case and a typical absorption curve of a thiocyanate is shown in Fig. 1. The absorption maximum is about 661 and the absorption ratio is 0.61.

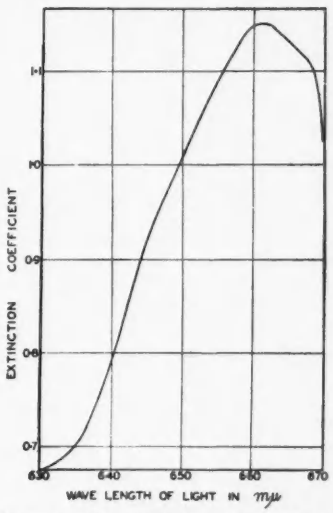


FIG. 1. *Absorption curve of methylene blue thiocyanate.*

Reduction Times in Milk

The methylene blue chloride used in the reduction test technique was in the standard tablet form, and Standard Methods of Milk Analysis (A.P.H.A., 1929) was followed. One part of methylene blue thiocyanate was added to 666,666 parts of milk, giving a depth of blue approximating that observed in the standard test. In each case a modified technique supplemented the standard test. This modification—the tubes were shaken hourly during incubation—tends to eliminate gross variations in the reduction times of replicate samples (9). The reduction times are reported in hours and minutes —thus 6:15 means 6 hr. and 15 min. It is probable that the reading of such color tests is frequently not accurate to within 15 min., especially in the analysis of the higher grade milks.

**The term absorption ratio is the ratio of the extinction coefficients at two specific wave-lengths, viz., 635 mμ and 665 mμ for methylene blue chloride.*

TABLE II

COMPARATIVE REDUCTION TIMES OF METHYLENE BLUE CHLORIDE AND METHYLENE BLUE THIOCYANATE IN MILK

Milk No.	Standard		Modified	
	Chloride	Thio-cyanate	Chloride	Thio-cyanate
1	6:15	6:05	4:30	4:30
*2	7:05	7:04	5:30	5:30
3	7:15	7:15	4:45	4:45
4	7:15	6:15	4:30	4:30
5	7:45	7:15	6:00	5:55
6	7:45	7:15	5:45	5:45
7	7:45	7:45	5:00	5:00
8	8:00	7:55	6:45	6:45
9	8:00	8:00	6:45	6:45
10	9:15	9:45	7:30	7:20
11	9:30	9:15	7:00	7:00
*12	9:57	9:23	6:30	6:30
Average	7:59	7:46	5:53	5:51

Average for five determinations.

The standard reduction times for the 12 milks listed in Table II show an average difference of 13 min. between the reduction time of the chloride and that of the thiocyanate. This is within the experimental error for this grade of milk, which statement is confirmed by the average difference of two minutes when the modified technique was employed. These data show that in this concentration methylene blue thiocyanate may be substituted for the present methylene blue chloride with no resultant changes in reduction times.

Oxidation-Reduction Potentials in Milk

The fact that in the same approximate concentrations in milk, methylene blue thiocyanate and methylene blue chloride reduction times are identical suggests that,

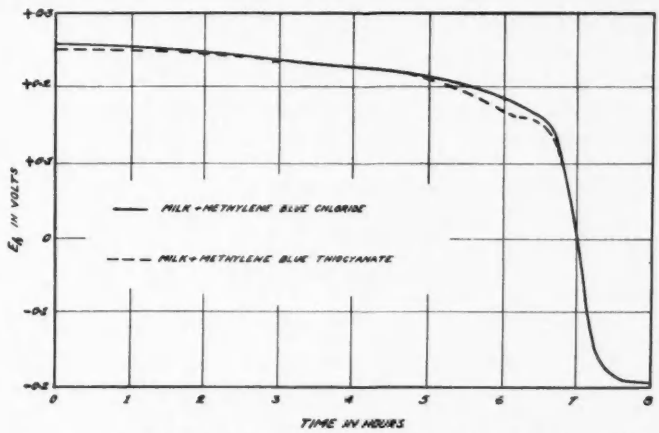
(*a*) The oxidation-reduction potential range over which the thiocyanate is reduced in milk closely approximates that over which reduction of the chloride is effected.

(*b*) The poising effects of the two dyes are not essentially different.

(*c*) Their lethal actions are similar.

So little is known of the lethal effect of methylene blue chloride in milk that it is at present impossible to compare the antiseptic or disinfectant properties of the two salts. Increased concentration of either results in a lengthening of the reduction time, and it is believed that this is due partly to lethal and color effects and partly to poising.

For the measurement of oxidation-reduction potentials in milk the usual apparatus, which included a Leeds and Northrup Type K2 potentiometer, a saturated calomel half-cell and platinum electrodes, was employed. Potentials in milk were measured at a temperature of 37° C. $\pm$ 0.5°. Time-potential curves, shown in Fig. 2, represent the potentials set up at electrodes in two tubes of the same milk, one containing methylene blue chloride in the standard concentration, and the other, methylene blue thiocyanate in a concentration of 1 : 300,000. Despite this high concentration of the thiocyanate the poising effect was no greater than that of the standard dye.



IG. 2. *Time-potential curves of methylene blue chloride and methylene blue thiocyanate in milk.*

Because the potentials set up at an electrode immersed in a tube of milk are frequently not representative for the entire contents of the tube, it was impossible to determine with accuracy the potential range over which reduction took place in milk. All observations pointed to the reduction of thiocyanate over the same approximate range as that of the chloride.

Oxidation-Reduction Potentials in Aqueous Solutions

A study of the oxidation-reduction potentials of methylene blue thiocyanate in aqueous solutions was also of importance. This work was carried out with the standard equipment already described in the section on oxidation-reduction potentials in milk. It should be mentioned here that a high degree of accuracy, such as that obtained by previous workers (1) with chloride systems, is not claimed.

Potentials in aqueous systems were determined by a titanous chloride titration of 0.0002 *M* thiocyanate solutions, taking all the precautions already mentioned. To keep the pH as constant as possible, the acidity of the titanous salt solution was determined, and then sufficient 0.5 *M* hydrochloric acid was added to a known amount of the dye solution to make a solution of exactly the same acidity as that of the titanous salt solution. However, this procedure does not necessarily ensure a constant pH, but it is believed by the authors that for this work it is sufficiently accurate. Again, the reader's attention is called to previous work in this field (1, 2, 7). It is hoped to repeat this work using highly buffered solutions containing known amounts of reductant and oxidant, the reduced solution being obtained by the use of hydrogen and a platinum catalyst.

In Fig. 3 are shown two typical curves representing the titration of 0.0002 *M* solutions of the chloride and thiocyanate, 0.2094 *M* with respect to hydrochloric acid, at 25° C. ± 0.1°. The half-cell was a saturated calomel electrode. From these curves the end point of the titration is determined. In Fig. 4, the per cent reduction for the two solutions is plotted against E_h. The E_h value at 50% reduction gives the E_0 at a pH that is approximately 0.7, as determined by the hydrogen electrode. Both the chloride and thiocyanate give E_0 values that are almost identical, *viz.*, 0.467 volts.

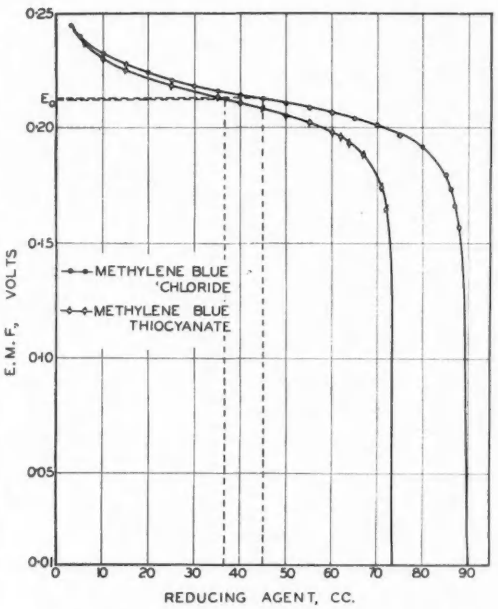


FIG. 3. *Electrometric titration curve for methylene blue chloride and methylene blue thiocyanate.*

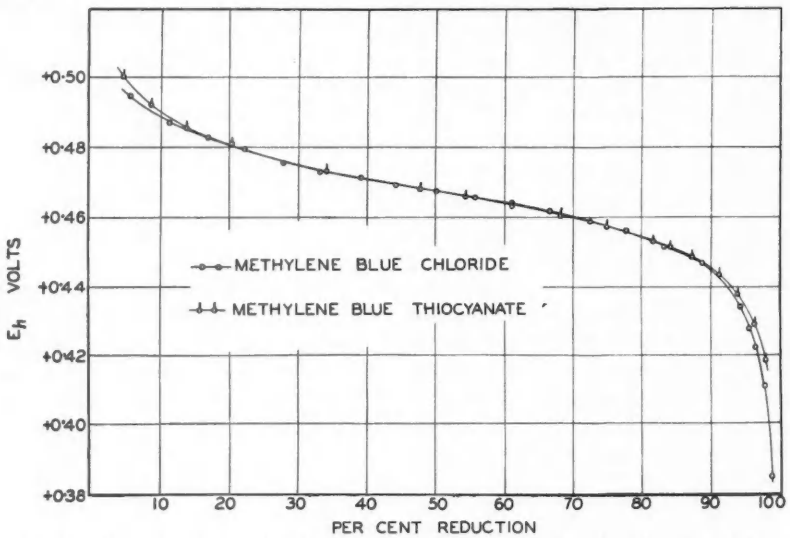


FIG. 4. *Degree of reduction-potential curves for methylene blue chloride and methylene blue thiocyanate.*

Methylene Blue Thiocyanate as a Stain

Methylene blue thiocyanate has been substituted for methylene blue chloride in the usual staining procedures in a course in general bacteriology without any observed disadvantages. These techniques, however, did not depend upon polychrome properties of the dye. The thiocyanate has been used extensively as a stain in the Breed method of preparing milk smears, and is preferred for this purpose because of the absence of troublesome precipitates. Solubility studies have not been made, but it has been observed by the authors and others that the thiocyanate salt is considerably less soluble in both water and alcohol than is the chloride.

Summary

The standardization of the methylene blue reduction test for bacteriological quality in milk requires the use either of an easily purified dye or one the purity of which is easily determined. Methylene blue thiocyanate is preferable to methylene blue chloride for this test because:—

1. Methylene blue thiocyanate is easily prepared in a state of purity approaching 100%, as shown by titanous chloride titration and spectrophotometric measurements.

2. It reduces over the same oxidation-reduction potential range as the chloride when in aqueous solution and probably when in milk.

3. The poising and lethal effects of the two dyes are not essentially different.

4. When present in approximately equal concentrations, the two dyes have the same reduction times in milk.

Acknowledgments

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THE NON-PROTEIN NATURE OF A FRACTION OF SOIL ORGANIC NITROGEN[1]

By A. W. J. Dyck[2] and R. R. McKibbin[3]

Abstract

It is shown that not all the nitrogen in organic soils is determinable by the Kjeldahl method. In every sample tested the Dumas method gave a considerably higher percentage of nitrogen.

The differences in nitrogen content, as shown by the two methods, vary from 6.4 to 29.6%, hence it is believed that an appreciable fraction of the soil organic nitrogen may be of non-protein nature.

Introduction

Two processes are apparent in the soil: (i) the process of formation of soil organic matter by the decomposition of plant residues and the subsequent accumulation of the decomposition products; (ii) the process of destruction of soil organic matter.

In the process of decomposition of plant residues, the loss of carbon exceeds that of nitrogen, and soil organic matter is considerably higher in nitrogen than the original plant materials. Plants vary widely on different soils qualitatively and quantitatively; their decomposition is brought about by the action of various micro-organisms under different climatic conditions; hence qualitative differences in the composition of soil organic nitrogen compounds may be assumed, *a priori*.

The importance of obtaining knowledge of the forms in which organic nitrogen exists in soils is obvious. It was thought that a comparison between the nitrogen content of soils obtained by the standard Kjeldahl and Dumas methods might be of value, and possibly could point to the nature of the nitrogen compounds in the soils.

Review of Literature

It is believed by many workers that soil organic nitrogen exists largely or totally in the form of proteins. Schmuk* believes that 60–80% of the total nitrogen in the soil belongs to the protein fraction. Remesow and Werigina (3) report that all the nitrogen which is hydrolyzed by hydrochloric acid is of protein nature. They base their conclusions on the analogy of the nitrogen distribution in proteins and the hydrolyzates of chernozem and brown earth soils.

	Amido nitrogen	Mono-amino nitrogen	Diamino nitrogen
"Protein"	9	67.32	25.2
Soil hydrolyzate	9.6	66.9	23.4

Laterite soils according to Remesow and Werigina (3) do not show this analogy.

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See Reference (3).

The fact that not all of the nitrogen in soils is hydrolyzed by mineral acids has often been brought forward as an argument that a considerable fraction of this nitrogen is of non-protein nature, but is present in the form of ring nitrogen compounds.

Waksman and Iyer (6) prepared artificial humus from casein and lignin, and compared the extent of hydrolysis of these preparations with that of natural humus. Table I shows their results.

TABLE I

	Unhydrolyzed residue	Per cent of protein nitrogen hydrolyzed
Casein	6.8	80.6
Lignin	94.3	3.2
H-ligno-proteinate	89.3	32.9
Ca-ligno-proteinate	80.3	20.2
Humus from peat	83.0	29.9

It may be seen from the table that natural humus is intermediate between H-ligno-proteinate and Ca-ligno-proteinate, and thus behaves in the same manner as the artificial "humus" preparations.

The behavior of artificial humus preparations toward acetyl bromide, according to Waksman and Iyer (6), is analogous to that of natural humus. They found that whereas proteins are completely, and lignin almost completely, dissolved by acetyl bromide, the artificial humus preparations, like natural humus, were attacked only to a limited extent. Their conclusion is that the non-hydrolyzed nitrogen fraction belongs to the proteins bound in some stable lignin complex.

Other workers have recognized the non-protein nature of a part of the soil nitrogen. Snyder and Potter (5) report an "unknown soluble non-protein nitrogen fraction." They estimated the amount of this fraction as 96–99% of the total nitrogen extractable by a 1% solution of hydrochloric acid. Dragunow (1), working on peats, reports complete absence of the diamino nitrogen fraction in the hydrolyzates.

It is well known (2, 4) that the nitrogen in compounds such as pyridine, quinoline, and their derivatives, and in certain compounds where nitrogen is linked to nitrogen, is not accounted for by the Kjeldahl method. It would follow, therefore, that, if such compounds are present in the soil in considerable amounts, the Dumas method for nitrogen determination should give higher results than the Kjeldahl.

Experimental

Materials

The samples analyzed were taken from widely different locations in the province of Quebec.

Methods

Nitrogen determination by the Kjeldahl method. (*a*) To 2-gm. samples of the soil, 7 gm. of a mixture of 5% copper sulphate (pentahydrate) and 95% potassium sulphate was added, and the whole digested with 30 cc. of concentrated sulphuric acid for 2–3 hr. The ammonia was distilled into 0.1 *N* hydrochloric acid solution.

(*b*) In the case of the hydrolyzates, 10 cc. was measured out into a Kjeldahl flask, 7 gm. of a mixture of 5% copper sulphate (pentahydrate) and 95% potassium sulphate, and 25 cc. of concentrated sulphuric acid were added. The whole was digested 2–3 hr., and the ammonia distilled into 0.01 *N* hydrochloric acid solution.

Nitrogen determination by the Dumas method. (*a*) A portion (0.3 gm.) of the finely powdered sample was mixed with 5 gm. powdered cupric oxide and ignited in a Vitreosil tube 36 in. long, the usual precautions being strictly observed.

(*b*) In the case of the hydrolyzates, 2 cc. of the solution was measured from a microburette into the boat containing the cupric oxide. The combustion was carried out much more slowly, as a disproportionate amount of steam was being evolved.

Blank determinations on 0.3 gm. of sucrose gave 0.15 cc. nitrogen gas. This value was subtracted from the volume of nitrogen collected in each of the above determinations.

Hydrolysis. A portion (100 gm.) of the soil was refluxed for 20 hr. with 500 cc. of 20% hydrochloric acid solution. The mixture was poured into a Büchner funnel and filtered with moderate suction. The first part of the filtrate usually came through turbid and had to be refiltered. The residue was washed five times with 50-cc. portions of hot 20% hydrochloric acid solution, followed by washing five times with 50-cc. portions of boiling distilled water. The filtrate was made up to one litre with distilled water, and the nitrogen determined as shown above.

The non-hydrolyzed fractions were dried in an oven at 100° C. and weighed. They were then ground to a fine powder and the nitrogen determined as shown above.

Results

Tables II and III show the results obtained.

TABLE II

Soil	% nitrogen, Kjeldahl method	% nitrogen, Dumas method	Soil	% nitrogen, Kjeldahl method	% nitrogen, Dumas method
Surface soil muck			*Subsoil muck*		
1	1.28	1.56	13	1.50	1.65
2	1.42	1.98	14	2.40	3.41
3	1.54	1.91	15	1.76	2.00
4	2.47	3.28	16	1.86	2.16
5	1.88	2.01	17	1.89	2.50
6	2.21	2.70	18	2.20	3.12
7	1.91	2.21	19	2.62	3.63
8	2.54	2.78	20	2.15	2.76
9	2.69	2.94	21	1.43	1.62
10	1.63	2.02	22	2.17	2.57
11	1.50	1.82	23	1.83	2.48
12	2.07	2.54	*Raw humus*		
			24	1.47	1.92
			25	1.52	1.86
			26	1.43	1.68

TABLE III

Soil	% nitrogen, Kjeldahl	% nitrogen, Dumas	N_2 expressed as % of total Dumas nitrogen of soil			
			N_2 of hydrolyzate		N_2 of residue	
			Kjeldahl	Dumas	Kjeldahl	Dumas
Surface muck						
1	1.28	1.56	52.37	64.59	26.44	36.73
2	1.42	1.98	50.28	68.40	22.05	31.28
3	1.54	1.91	58.29	73.21	24.53	27.76
Subsoil muck						
13	1.50	1.65	58.17	64.19	28.82	36.36
22	2.17	2.57	57.80	69.39	21.49	30.64
23	1.83	2.48	50.31	63.40	29.60	36.19
Raw humus						
24	1.47	1.92	58.35	80.20	18.46	18.99
25	1.52	1.86	64.40	74.49	14.36	25.16
26	1.43	1.68	65.35	80.12	19.37	19.49

Discussion

The results in Table I show that there are considerable differences in the percentages of nitrogen in organic soils as determined by the Kjeldahl and the Dumas methods. In the soils examined 6.4–29.6% of the total nitrogen is non-determinable by the Kjeldahl method. It is not the authors' intention to attempt to prove or disprove the protein nature of the fraction which is determined by the Kjeldahl method, but it would seem that that fraction which can be determined only by the Dumas method cannot very well be classed in the ordinary sense as "protein" nitrogen, because of its enormous stability toward sulphuric acid digestion. This fraction might exist as ring nitrogen or as nitrogen in the form of some stable compounds in which nitrogen is linked to nitrogen.

The question might occur as to whether Waksman's "ligno-protein complex", which is stable toward mineral acid hydrolysis, may not be responsible for the difference. However, upon inspection of Table III, it will be seen that there is a difference between the nitrogen contents of the hydrolyzates as well as between those of the non-hydrolyzed residues. Furthermore, there are two cases, the raw humus samples numbered 24 and 26, where the nitrogen content of the non-hydrolyzed fraction, determined by the Kjeldahl method, is equal to that of the Dumas method. This appears to exclude the likelihood that Waksman's "ligno-protein complex" is the cause of the difference in nitrogen content shown by the two methods.

It seems obvious that the nitrate nitrogen should have no effect on the difference. In the extreme case, owing to the small amounts present in these soils, it would account for only a negligible fraction of the soil nitrogen. In soils with a carbon content of 0.8% or higher, it is believed that all of the nitrate nitrogen is determined by the ordinary Kjeldahl method. The carbon content of the soils studied far exceeds the 0.8% limit.

From the results it will be seen that the Dumas method gives higher results for nitrogen in the hydrolyzates.

The conclusion of Remesow and Werigina, that the nitrogen compounds in the hydrolyzates are 100% amino acids, is believed to be invalid.

Similarly, the Dumas nitrogen values of the non-hydrolyzed fractions, except in two cases, indicate that this fraction is not, as Waksman and Iyer believe, wholly of protein nature.

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SOME CONSTITUENTS OF THE SAP OF THE SUGAR MAPLE (*ACER SACCHARUM*, MARSH.)[1]

By G. H. Findlay[2] and J. F. Snell[3]

Abstract

Skazin's observation that maple flavor is not present as such in sugar maple sap but develops at boiling temperatures (100–104° C.) has been confirmed. Levorotatory glucosides cannot be detected in sap concentrated to 1/150 its volume, and are therefore probably not present in amounts exceeding 1 gm. (calculated as coniferin) per 50 litres. In maple wood, pyrocatechol tannins were detected but no alcohol-soluble glucosides. The sap contains succinic acid, a glucosidase, an unsaponifiable oil, a water-soluble substance melting at 191.5° C.* and having the composition $C_{11}H_{21}O_9$, and an acetone-soluble substance giving lignin-like color tests. Maple flavor could not be developed in any individual constituent of the sap.

Introduction

Attempts to associate the characteristic flavor of maple syrup and maple sugar with a definite constituent have been only partially successful. Nelson (8) and also Skazin and Snell (14; 15, p. 56) have reported the isolation in minute quantity of an aldehyde resembling vanillin in its odor, and have described some of its properties. They have extracted a larger quantity of an unstable phenolic substance which appeared to be *chiefly* responsible for the flavor. Risi and Bois (10, 11) have expressed the opinion that the aroma is due to a substance of rather saturated nature (less readily oxidized by permanganate than is malic acid), and Labrie (7), working under Risi (12), concluded that the flavoring principle was identical with the material "hadromal," obtained from wood by Czapek (4) and Hoffmeister (6), and associated by the last-mentioned with ferulic aldehyde, the aldehyde of coniferyl alcohol. The standing of hadromal as a chemical compound has not been definitely established (5, 9), though Combes (3) attributed certain histological behavior of lignified tissue to it, and Labrie inferred from odor and absorption spectrum observations that it could be synthesized from vanillin, guaiacol and sucrose (through furfural).

Development of Maple Flavor

It was demonstrated by Skazin (14) that the characteristic flavor of maple syrup and sugar is not present in the sap, but is developed during the boiling. The authors have confirmed this conclusion. The evidence is as follows:

1. Concentration of sap at temperatures lower than the boiling point—*viz.*, by vacuum distillation or by partially freezing out the water and completing the concentration *in vacuo*—produced a syrup with a mild flavor resembling that of watermelons rather than the true maple flavor.

[1] *Manuscript received August 10, 1935.*
Contribution from the Chemistry Department of Macdonald College, Macdonald College P.O., Quebec, Canada. Macdonald College Journal Series No. 67.
The experimental results are presented in more detail in a thesis submitted in September, 1934, in conformity with the requirements for the degree of Doctor of Philosophy in McGill University.
[2] *Canadian Industries Limited, Beloeil, Que., formerly Assistant in Chemistry, Macdonald College.*
[3] *Professor of Chemistry, Macdonald College.*
* *All melting points are corrected.*

2. Refluxing at atmospheric pressure developed true maple flavor in the syrup prepared as described above.

3. Heating the vacuum-produced syrup to 105° C. in a sealed tube caused development of true maple flavor.

4. Refluxing of sap at atmospheric pressure, followed by vacuum concentration, produced a syrup of true flavor.

5. Extraction of sap with ethyl acetate followed by concentration of the aqueous layer under atmospheric pressure produced a syrup without maple flavor.

6. Extraction of maple syrup with ethyl acetate did not remove the maple flavor, showing that it must be a precursor of the flavoring principle, and not the principle itself, that dissolves in the acetate.

7. Concentration of maple sap to dryness *in vacuo* yields a yellowish white product of woody flavor. Heated to 100° C. for one to two hours, this product develops a light brown color and the maple flavor.

Search for Glucosides

That the development of the flavor from its precursor is not an oxidation process is evidenced by the fact that as good a flavor can be developed in an atmosphere of carbon dioxide as in the air. In preliminary (unpublished) work in this laboratory, E. E. Massey also produced the flavor by refluxing vacuum-produced syrup in an atmosphere of hydrogen, while heating such syrup with one-tenth its volume of 3% hydrogen peroxide in a sealed tube produced a flavor different from that of maple syrup.

The possibility that the flavoring substance might be liberated from a glucosidic compound by hydrolysis suggested itself. Examination of the data of Bryan (2) revealed no correlation between flavor and invert sugar content. An equal number of syrups of the lowest invert sugar content were classified by him as of "good" and of "mild" flavor, and the same holds true of the syrups of high invert sugar content. Moreover, the one syrup amongst his 481 in which Bryan found no invert sugar was classed as of "fair" flavor. As these estimates of invert sugar were based on reduction of Fehling's solution, no support is afforded for the conjecture that the flavor may be produced by the hydrolysis of a glucoside during the boiling.

However, tests for glucosides by Bourquelot's "biochemical" method (13) were carried out upon fresh sap, sap concentrated *in vacuo* with and without previous freezing, and upon alcohol extracts of the cambium and sap wood of *Acer saccharum*. Bourquelot's test consists essentially in measuring both the polarization and the reducing power of the liquid before and after treatment with invertase and again after treatment with emulsin. If glucosides (levorotatory) are present the emulsin treatment should alter the rotation in the positive sense and also increase the reducing sugar content.

In tests made in the sugaring seasons of 1932 and 1933 on fresh sap and sap concentrated *in vacuo* or by freezing, good agreement was obtained between

the observed and calculated changes due to the invertase treatment, indicating that the sucrose was completely hydrolyzed and that the method of determining reducing sugars was reliable. In the emulsin treatment, the 1932 syrups showed slight increases in reducing sugars and positive rotation, but in the 1933 samples changes in rotation varied from −0.14 to +0.1° and in reducing sugars from −0.55 to +0.03 gm. per 100 cc. As duplicate determinations of reducing sugars varied by the equivalent of 1 to 5 mg. of invert sugar, amounting to 0.05 to 0.25 gm. per 100 cc. of sap and 0.1 to 0.5 gm. per 100 cc. of syrup (13.5–30.0% solids), the observed variations are virtually within the limits of experimental error. Furthermore, the observed increases in reducing sugar and in rotation were no greater for the syrups (vacuum or freezing) than for the unconcentrated sap. Even in a concentrate prepared by removal of sucrose from a vacuum syrup by precipitation with alcohol and acetone (see below), the increase of reducing sugar amounted to only 0.20 gm. per 100 cc., and the change in rotation was in the negative direction. The concentration of flavor precursor in this concentrate should be 150 times that in the original sap.

Sap wood and the cambium from the trunk of the maple tree were boiled with alcohol containing a little calcium carbonate, the filtrate evaporated, taken up in water and subjected to treatment with invertase followed by emulsin. Again no evidence of alcohol-soluble glucosides was obtained.

If the development of maple flavor were due to hydrolysis of a glucoside, reducing sugars should be increased in amount by refluxing sap or sap concentrated at lower temperature. The results in Table I, obtained by refluxing for one to three hours, show that no measurable increase occurs.

TABLE I

CHANGES IN REDUCING SUGAR CONTENT OF MAPLE SAPS DURING REFLUX BOILING

Sample	Total solids, %	Invert sugar, gm. per 100 cc.		
		Before refluxing	After refluxing	Change
Sap A	3.5	0.014	0.021	+0.007
Sap B	3.7	0.033	0.027	−0.006
Sap concentrated by freezing	23.0	0.254	0.235	−0.019

It may be calculated from the specific rotations of sucrose and of the glucoside coniferin, which has been regarded as a possible source of maple flavor, that a concentration of 0.3 gm. of the glucoside per 100 cc. would be necessary to yield a conclusive change in optical rotation upon hydrolysis with emulsin. Accordingly, although all the authors' experimental evidence is against the existence of a glucoside in maple sap, the possibility of the presence of such a substance in a concentration lower than 0.002 gm. per 100 cc. (1 gm. in 50 litres) is not excluded.

Extraction of Wood

Freshly cut shavings of the cambium and sap wood of the trunk of a sugar maple cut during the 1933 sugaring season were refluxed 30 min. with the following solvents: water, ethyl acetate, amyl alcohol, petroleum ether. The solutions were concentrated (*in vacuo*, except the petroleum ether extract), any solid sediment filtered out, and the filtrate further concentrated to approximate dryness.

The residues were amorphous except that from petroleum ether, which was very small in quantity (0.01–0.02 gm. per 100 gm. of wood) and melted at 125-130° C. Ethyl alcohol yielded the largest amount of amorphous extract (0.83 and 1.07 gm. per 100 gm. of wood), amyl alcohol the next (0.25 and 0.85 gm.) and ethyl acetate the next (0.25 and 0.30 gm.). No evidence of the presence of coniferin was obtained. The extracts obtained with water and the two alcohols, when taken up in water, responded to Molisch's, Fehling's, Seliwanoff's and Froehde's (molybdic acid) tests. Barfoed's test was also given by the water and ethyl alcohol, and by one of the amyl alcohol, extracts. The petroleum ether and ethyl acetate extracts, however, responded to none of these tests. It may be inferred that the wood contained sucrose and that a monosaccharose was either originally present or produced during the extraction. This monosaccharose yielded glucosazone and must therefore have been glucose, fructose or mannose.

From the water extract, tannins were precipitated by cinchonine sulphate and identified as pyrocatechol derivatives by color and precipitation reactions and by fusion with potassium hydroxide (1).

Vacuum distillation products. In 1933, 8.7 litres of syrup, and in 1934, 13.8 kilos of sugar, were prepared by evaporation of sap at 37–45° C. under reduced pressure. The color of the products was light yellow, the taste sweet and somewhat astringent but not suggestive of maple flavor. Heating the sugar to 100° C. in an oven darkened the color and developed the maple flavor, while neither effect was produced in a parallel experiment with cane sugar. The sugar contained 0.89% of ash, 0.02% of nitrogen and had a pH of 6.1, measured electrometrically in a solution of 20 gm. in 100 cc.

A hydrolytic enzyme. Labrie (7) discovered in maple bark an enzyme ("acerase") capable of hydrolyzing coniferin and amygdalin. He also obtained evidence of an amylase in the sap of the tree.

The authors have found that the addition of tannic acid solution to a solution of vacuum syrup or sugar, but not to ordinary maple syrup nor to refluxed vacuum syrup, results in the gradual development of a purple color. On boiling, a purple coagulum is produced.

With solutions of known enzymes, *viz.*, emulsin, invertase, maltase and trypsin, tannic acid was found to give a light mauve coloration and a precipitate on standing. This color test was given by vacuum sugar, which had been extracted with ethyl acetate, ether or acetone, and also by sugar precipitated from vacuum syrup by alcohol. The substance responsible for the

reaction would, therefore, appear to be insoluble in these solvents. It was also removed from aqueous solution by treatment with charcoal or with Lloyd's alkaloidal reagent (hydrated aluminium silicate). No precipitate was given with Millon's reagent, copper sulphate, mercuric chloride (without or with hydrochloric acid) and no color was developed in the biuret test. A positive xanthoproteic reaction was obtained in vacuum syrup, but this was given also by ordinary maple syrup. The enzyme was still present in a solution that had been treated with lead acetate, filtered and freed from lead by addition of sodium carbonate.

One hundred grams of vacuum sugar was ground with 300 cc. of glycerol, allowed to stand 24 hr., centrifuged and decanted. To the glycerol extract, three times the volume of 95% alcohol was added. On standing, 0.048 gm. of flocculent, dirty-white solid (dried *in vacuo* over sulphuric acid) was obtained. This material contained 1.76% of nitrogen and 32.7% of ash. It dispersed in water, forming a turbid mixture which gave the purple color with tannic acid and a purple ring with α-naphthol and sulphuric acid, but no xanthoproteic, glyoxylic or biuret test.

Amygdalin, arbutin, salicin and cane sugar in 0.5% solution incubated at 35° C., with and without addition of a portion of the enzyme, showed no reducing sugar after three days, but at the end of a week the solutions containing the enzyme gave slight Fehling tests while the blanks gave none.

Whether this enzyme is identical with Labrie's "acerase" cannot be definitely stated.

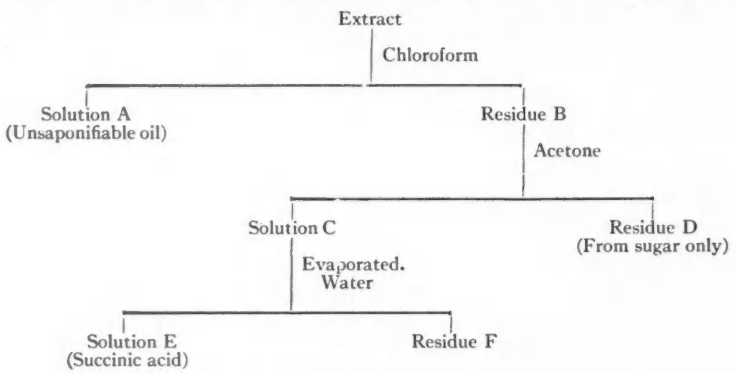
Alcohol-soluble products. It was thought that the flavor precursor might be obtained in more concentrated form by removal of sucrose from vacuum syrup by precipitation with alcohol, or by extraction of vacuum sugar with solvents in which sucrose is insoluble.

1. *Treatment as syrup.* The syrup was further concentrated *in vacuo* to a solids content of about 80% and treated, while still warm, with twice its volume of 95% alcohol, and shaken continually until the sucrose had separated in granular form and then intermittently until cold. The sucrose was filtered off and washed with alcohol. About 80% of the sucrose was thus removed. The alcoholic solution was then evaporated *in vacuo* to a syrup and either (i) extracted with other solvents or (ii) still further evaporated and treated with alcohol or (better) acetone to again reduce the sugar content, and once more concentrated *in vacuo*. The concentrate obtained from 8.7 litres of vacuum syrup after a second precipitation of sucrose amounted to 450 cc. Glucosides, if present, were not in sufficient quantity for detection by Bourquelot's method. Maple flavor could be developed by boiling. Extracts of this concentrate made by shaking it successively with ethyl acetate, ether and amyl alcohol were concentrated by evaporation—*in vacuo* except the ether extract—and treated in the same manner as the extracts of vacuum sugar.

2. *Treatment as sugar.* Fresh sap, 240 litres, of early run and high sugar content (5–6% by refractometer) was distilled to approximate dryness *in vacuo*

at temperatures of 37–45° C. This sugar, of which 13.8 kilos (air-dry) was obtained, was found to yield very little extract to benzene, chloroform or petroleum ether. Acetone dissolved some of the sugar. The best solvents for the non-sugars were ethyl acetate and ether. Extraction with these solvents was carried out in an improvised Soxhlet apparatus capable of handling 500 gm. of solid and one litre of solvent. The extraction was continued for six hours and each portion of solvent was used on four batches of sugar. Four kilograms was extracted with ether, followed by ethyl acetate, and seven kilograms, with ethyl acetate alone. After the ether extract had been concentrated to a volume of 10 cc. it yielded 0.38 gm. of succinic acid and an unsaponifiable oil. The succinic acid melted at 185° C. and its equivalent weight was 56.57 (theory 59). It gave an insoluble silver salt, a red color and—on boiling—a precipitate with ferric chloride, and a white sublimate (anhydride). The unsaponifiable oil remained liquid at 0° C., gave no color reaction with ferric chloride or phloroglucinol–hydrochloric-acid, and had no apparent relation to maple flavor.

The separation of the materials extracted from vacuum syrup and vacuum sugar by ethyl acetate was conducted according to the following flow-sheet.



The oil A resembled that obtained from the ether extract of the sugar, except that it was more viscous and had an acid odor, doubtless due to hydrolysis of the ethyl acetate during concentration. Residue D obtained from the sugar (1934 crop) but not from the syrup (1933 crop), when recrystallized from alcohol, formed colorless, monoclinic prisms, insoluble in ether, slightly soluble in ethyl alcohol and in ethyl acetate, easily soluble in water. Weight 56 mg., m.p. 191.5° C. Found: C, 44.1, 44.1; H, 7.2, 7.1; $OCH_3+OC_2H_5$, 15.1%. Calcd. for $C_{11}H_{21}O_9$: C, 44.4; H, 7.1; OC_2H_5, 15.1 or $(OCH_3)_2$, 16.0%.

The aqueous solution gave no color with ferric chloride, with phloroglucinol–hydrochloric-acid, nor with the Folin-Denis reagent for phenols, no Molisch test and no precipitate with lead acetate. No relation of this substance to maple flavor was observed.

Succinic acid was identified in Solution E by the same tests used with the ether extract, equivalent weights of 58.2 and 58.5 being obtained.

Residue F, a light, yellowish brown powder, was soluble in alcohol, acetone and acetic acid. It also dissolved in dilute ammonia and was reprecipitated upon acidification. It gave color reactions resembling those attributed to lignin, *viz.*, red with phloroglucinol–hydrochloric-acid, orange with benzidine–hydrochloric-acid, yellow with aniline–hydrochloric-acid, deep blue with the Folin-Denis reagent and no color with ferric chloride. The methoxyl values of the residues from the syrup and sugar were discordant, *viz.*, 16.3 and 10.2%.

Although these color tests suggest a relation between maple flavor and lignin (7), it was not found possible to produce maple flavor from this lignin-like material by adding it to dilute sugar solution and boiling to a syrup. On the other hand, no maple flavor could be developed in the extracted sugar by heating it or its solutions. Thus no definite precursor of maple flavor has been isolated in this work, and it would seem possible that, as contended by Labrie, the flavor may be due to interaction of sucrose or a product thereof with other constituents.

Acknowledgments

The maple syrup and sap were obtained through a grant of the Quebec Department of Agriculture to Macdonald College. The refrigerator and microchemical apparatus used were the property of the National Research Council and the privilege of using them is gratefully acknowledged. The authors wish to thank Dr. C. F. H. Allen of McGill University, and Mr. L. Skazin of the National Research Laboratories for valuable suggestions.

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THE SOLUBILITY OF LIME IN WATER[1]

By G. L. Larocque[2] and O. Maass[3]

Abstract

The solubility of lime has been determined with a high degree of accuracy over the temperature range 0 to 30° C. by a conductivity method. The degree of dissociation of lime over this temperature range and over the concentration range 0 to 1.164 gm. of calcium oxide per litre has been calculated.

Introduction

As part of the elucidation of the equilibria existing in sulphite cooking liquor (the system calcium-oxide–sulphur-dioxide–water), it was necessary to determine the solubility of lime in water, and the conductivity and degree of dissociation of its saturated solutions. Exact solubility values were also required in lime sorption measurements on cellulose which will be described in a subsequent paper.

Grieve, Gurd and Maass (1) have made a survey of the existing literature and have compared the mean value so obtained with values measured by means of their new conductivity technique, which enables measurements to be made on solutions free from contamination by carbon dioxide. In the present investigation their measurements have been repeated and extended, using their identical method, and values have been obtained for the temperature range 0° to 30° C.

It is characteristic of this method that the solubility values are calculated from conductivity measurements that are virtually unaffected by the presence of colloidal particles, which would seriously affect a gravimetric analysis.

Procedure and Results

In the present work, the apparatus, materials and procedure were the same as those employed by Grieve, Gurd and Maass (1), and are fully described by them.

Solubility Measurements

The method consists essentially in measuring the electrical conductivity, at temperatures from 0° to 30° C., of a series of lime solutions of known concentration, and of a solution having an excess of lime present. These results are given in Tables I and II.

[1] *Manuscript received August 20, 1935.*
Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Quebec, Canada.

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TABLE I

SPECIFIC CONDUCTIVITY MEASUREMENTS

Conc'n., 0.124		Conc'n., 0.564		Conc'n., 0.724		Conc'n., 0.842		Conc'n., 1.164	
Temp., °C.	k	Temp., °C.	k	Temp., °C.	k	Temp., °C.	k	Temp., °C.	k
0.10	5.05	0.06	25.08	0.01	29.82	0.10	36.67	0.15	48.41
4.60	5.77	6.16	29.34	8.43	38.72	4.55	40.84	6.15	55.54
10.23	6.78	11.65	33.08	15.47	45.03	9.55	45.80	10.50	62.08
15.42	7.42	20.29	39.19	22.54	51.18	15.55	51.81	17.28	69.90
22.35	8.49	23.01	41.14	31.04	58.72	22.01	58.15	21.78	75.58
29.15	9.51	24.73	42.41			30.10	66.34	29.04	85.15
		30.00	45.97						

NOTE:— *The concentrations are expressed in grams of calcium oxide per 1000 gm. of water and the specific conductivities in reciprocal ohms* $\times 10^4$.

TABLE II

CONDUCTIVITY OF SATURATED LIME SOLUTIONS

Saturated solution: equilibrium values		Saturated solution: temperature falling		Saturated solution: temperature rising	
Temp., °C.	k	Temp., °C.	k	Temp., °C.	k
0.10	57.40	6.42	65.59	8.17	69.43
14.15	73.83	7.12	66.51	8.99	70.26
29.12	89.79	7.65	65.97	12.53	74.63
29.26	89.80	13.80	73.72	18.50	80.89
30.65	90.19	14.28	73.60	19.81	81.84
		25.28	85.45	28.35	89.22

The measurements were carried out in a completely glass-enclosed system, free from air and carbon dioxide. From the conductivity values, isothermal curves, conductivity *versus* concentration for temperatures differing by 5° at intervals from 0° to 30°, were plotted. The concentration of the saturated solution for various temperatures was then determined by extrapolating each temperature curve until it cut a line drawn parallel to the concentration axis, and through the conductivity value of the saturated solution at that temperature. The solubility values obtained in this manner are given in Table III, together with the values obtained by Grieve, Gurd and Maass (1).

TABLE III

SOLUBILITY OF CALCIUM HYDROXIDE IN WATER (EXPRESSED AS GRAMS OF CALCIUM OXIDE PER LITRE)

Temp., ° C.	0	5	10	15	18	20	25	30
Calcd. values	1.456	1.430	1.404	1.370	—	1.333	1.284	1.230
Grieve, Gurd and Maass's values	1.55	—	1.45	—	1.34	—	1.25	—

In the case of the saturated solutions, the equilibrium between the solid calcium hydroxide and the aqueous phase at any fixed temperature is established very slowly, and this likely has been a common source of error in earlier determinations. For this reason, conductivity measurements have been made with rising and falling temperatures, the temperature being allowed to remain constant for 10 or 15 min. before the reading was taken. The results are given in Table II and are plotted in Fig. 1. The magnitude of the

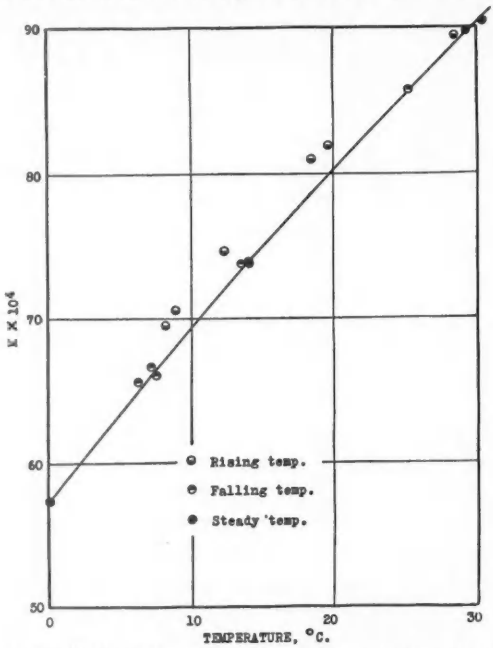

FIG. 1. *Conductivity measurements of a saturated lime solution.*

observed conductivity value is dependent on whether the equilibrium is reached when the temperature is rising or when it is falling, a final steady value being obtained only at the end of 6 to 12 hr.

In the case of those measurements made with a rising temperature, the tendency for supersaturation to occur in the system seemed to be greater than that for unsaturation when the final state was reached with a falling temperature.

Degree of Dissociation

It was of interest to determine the extent of the dissociation of the calcium hydroxide at different concentrations and temperatures. The conductivity measurements obtained with each of the five solutions used were plotted against temperature, and from these curves the conductivities at 0, 10, 20

and 30° C. were found by interpolation. The concentration of the ionized calcium hydroxide present at each concentration and temperature was then calculated from the specific conductivity, k, and the ionic mobilities of the Ca^{++} and OH^- ions by means of the relation

$$1000\,K = [Ca^{++}]u + [OH^-]v.$$

The concentration of the ionized calcium hydroxide having been calculated, the degree of ionization was then determined from the solubility values. The results are given in Table IV. It is to be observed that the degree of dissociation increases regularly with decrease in concentration and decrease in temperature.

TABLE IV

THE PER CENT DISSOCIATION AND HYDROXYL ION CONCENTRATION (IN GRAM IONS PER LITRE) OF CALCIUM HYDROXIDE AT VARIOUS CONCENTRATIONS AND TEMPERATURES

Conc'n., gm. CaO/litre	0.1024		0.564		0.724		0.842		1.164	
Temp., °C.	$[OH^-]$	%	$[OH^-]$	%	$[OH^-]$	%	$[OH^-]$	%	$[OH^-]$	%
0	0.0068	94	0.0344	86	0.0430	83	0.0500	83	0.0660	79.3
10	.0070	96	.0336	84	.0426	83	.0487	81	.0644	77.4
20	.0070	96	.0333	83	.0420	81	.0481	80	.0628	75.5
30	.0069	95	.0330	83	.0417	81	.0476	79	.0626	75.3

Grieve, Gurd and Maass (1), in their determination of the solubility, used two reference solutions of concentration 0.536 and 0.737 gm. of calcium oxide per litre, and extrapolated the conductivity values obtained to correspond to a saturated concentration of about 1.40. This extrapolation is too great to give values of sufficient accuracy for an investigation on the adsorption of lime which will be published in a subsequent paper. It was for this reason that the solubilities were redetermined by the authors.

In the present investigation, five solutions of concentration 0.1024, 0.564, 0.724, 0.842 and 1.164 were used, and, as a result, the solubility values obtained are considered to be correct to 0.008 gm. of calcium oxide per 1000 gm. of water over the temperature range 0 to 25° C. The order of accuracy is less for the degree of dissociation values, since the magnitude of the calcium ion mobility is known only to two significant figures.

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THE HEATS OF SOLUTION AND SPECIFIC HEATS OF RHOMBIC SULPHUR IN CARBON DISULPHIDE: THE SURFACE ENERGY OF SOLID RHOMBIC SULPHUR[1]

By A. R. Williams[2], F. M. G. Johnson[3] and O. Maass[4]

Abstract

The heats of solution of rhombic sulphur in carbon disulphide were measured over the concentration range 6 to 17% of sulphur and at 20° and 25° C., and the specific heats of these solutions were calculated. The apparatus designed for these measurements is described. By measuring the heat of solution of finely divided sulphur and its particle size, the surface energy of solid rhombic sulphur is estimated.

Introduction

Since the surface of a solid is so rigid that no appreciable movement towards minimum surface can occur, the measurement of the surface energy of a solid presents a problem altogether different from that involved in the measurement of the surface energy of a liquid. In the hypothesis that the surface energy of a solid is directly proportional to the surface of the solid, a way lies open to the solution of this problem. Thus, if a very large solid surface is produced by finely dividing a material, a measurable amount of surface energy will be produced in connection with this large surface. It is known that the surface energy so produced will manifest itself in various ways, such as in the increased vapor pressure or solubility of small particles or in the increase in the heat of solution of the finely divided solid. Centnerszwer and Krustinsons (7, 8) have attempted to measure this increase in vapor pressure of small solid particles over that of large solid particles and so calculate the surface energy of the solid. Dundon and Mack (9) have calculated the surface energy at the solid-liquid interface of some sparingly soluble solids from a measurement of the increased solubility of fine particles.

Bruzs (6) has attempted to measure the surface energy of a solid as the difference in the heats of reaction when one of the products of the reaction is produced in a finely divided state, and in the other case in a coarsely divided state.

Lipsett, Johnson and Maass (13, 14, 15) have obtained a value for the surface energy of a solid by measuring the difference between the heat of solution of coarsely crystalline, and that of finely divided, material.

Other investigators who have contributed something to the solution of the problem of the measurement of the surface energy of a solid are Jones (12), Hulett (11), Berggren (3) and Born and Stern (5).

[1] *Manuscript received July 25, 1935.*
Contribution from the Physical Chemistry Laboratory of McGill University, Montreal, Quebec, Canada, with financial assistance from the National Research Council of Canada.
[2] *Holder of a studentship under the National Research Council at the time the research was carried out.*
[3] *Dean of the Faculty of Graduate Studies and Research, McGill University.*
[4] *Macdonald Professor of Physical Chemistry, McGill University.*

Experimental

In the present research an attempt is made to measure the surface energy of the solid element sulphur. The method used is essentially the same as that first employed by Lipsett, Johnson and Maass in the measurement of the surface energy of sodium chloride. By this method the energy associated with the surface of a finely divided solid appears as a positive quantity in the difference between the heat of solution of very finely divided material and the heat of solution of coarsely crystalline material. From this difference in the heat of solution and from the measured difference in the areas of the coarse and the fine material, a simple arithmetical calculation gives the surface energy of the solid per unit area.

This difference in the heat of solution for the amount of solid surface produced is rather small, so that the heat of solution measurements have to be made very accurately. To obtain the required accuracy in the present research, an adiabatic calorimeter was used. The calorimeter is of the type described by Lipsett, Johnson and Maass and shown in Fig. 1. It consists essentially

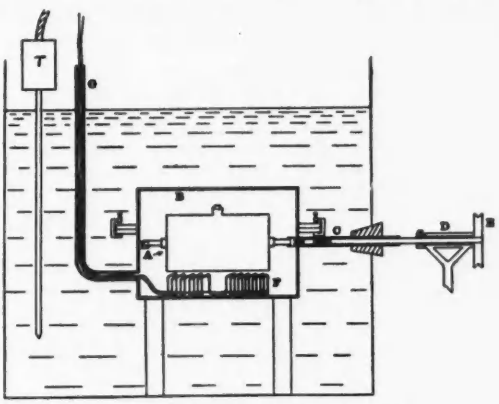

FIG. 1. *Adiabatic rotating calorimeter.*

of a small inner calorimeter, *A*, air-jacketed by means of a copper cylinder, *B*, and placed in a water bath. A 20 mm. air space insulates the calorimeter from the wall of the copper jacket. Within this small calorimeter, *A*, solute and solvent are placed in such a manner that when the calorimeter is rotated, the solute and solvent mix and solution takes place. During solution the outer bath is kept at the same temperature as the inner calorimeter, *A*. Thus when the temperature of the inner calorimeter is changing, owing to solution taking place, the temperature of the outer bath is made to change a corresponding amount.

In order to follow the temperature change of the inner calorimeter with that of the outer bath, the copper jacket is provided with a series of thermo-elements, *F*, which record the difference between bath and calorimeter tem-

perature. One set of junctions is blackened and placed about 1 mm. from the surface of the calorimeter, *A*. This set of junctions assumes the temperature of *A* by radiation. The other set of junctions lies along the bottom of the copper jacket, *B*. This set of junctions assumes the temperature of the outer bath by conduction. The thermo-elements are connected to a spot galvanometer. When both sets of junctions are at the same temperature, that is, when the bath and calorimeter are at the same temperature, there will be no deflection of the galvanometer spot. The temperature of the outer bath is controlled by addition of hot or cold water from small taps at the bath surface.

The temperature of the calorimeter is obtained by measuring the temperature of the outer bath. This is possible since by means of the thermo-elements the calorimeter and bath can be brought and kept to within 0.0001° C. of each other while temperature measurements are being made. The outer bath temperature is measured by means of a platinum resistance thermometer, *F*, which records temperatures to within 0.0002° C. Since the total temperature change during a heat of solution experiment is in the neighborhood of 1° C., this temperature-recording apparatus is capable of measuring temperature changes with an accuracy of 0.02%.

In measuring the heat of solution of sulphur it was necessary to use the volatile organic solvent carbon disulphide to dissolve the sulphur. Owing to the corrosive action of sulphur solutions on most metals, it was found necessary to build the small inner calorimeter from "Stabrite" steel, this material being unacted upon by sulphur solutions and in addition possessing the necessary property of good heat conductivity.* New features were required in this calorimeter as compared to the original calorimeter of Lipsett, Johnson and Maass (13, 14, 15), owing to the great volatility of the solvent, carbon disulphide, and also its solvent action on ordinary sealing media such as vaseline or other greases. To render the calorimeter leak proof a satisfactory sealing material was necessary, and this was obtained only after a long investigation.

The calorimeter was so designed that absolutely none of the volatile carbon disulphide could escape either in the liquid or gaseous state, thus eliminating the appreciable error that would arise from the cooling effect of escaping and evaporating carbon disulphide during the course of an experiment. The new features of the calorimeter are brought out in the following description.

The calorimeter is shown in Fig. 2. It is the small calorimeter indicated as *A* in Fig. 1. One end of the calorimeter is removable. This permits introduction and removal of the solute box. This removable end is designed primarily for tightness. Sixteen brass screws press a circular flange into a groove containing a lead gasket. The calorimeter axles are of bakelite, which is a poor heat conductor. Furthermore, bakelite is stronger than glass. The opening which is closed by means of the taper screw shown at the top of

* *The calorimeter was machined by Mr. Pye, Technician in charge of the Physics Department machine shop.*

the calorimeter serves for the introduction of the solvent after the solute box has been inserted and the removable calorimeter end tightened on. A quantity of solvent sufficient to bring its level halfway to the top of the solute box is introduced.

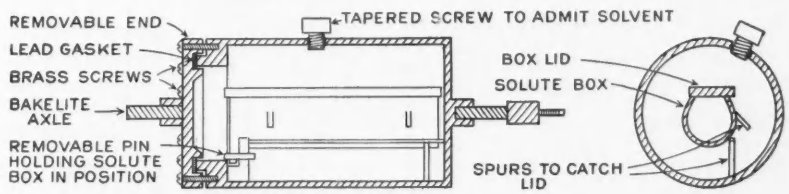

FIG. 2. *Inner calorimeter; A in Fig. 1.*

When the calorimeter is rotated, the solute box becomes inclined and the lid slips from the box opening. The open box containing the solute then dips into the solvent and solution occurs. Rotation of the calorimeter aids in rapid solution. A heating effect caused by the lid tumbling in the rotating calorimeter is eliminated by means of spurs on the side of the box which catch and hold the lid. In order to provide the snug fit that was essential for keeping the solvent vapor from the solute until the proper time for solution, the box lid was ground to the box opening. A sealing medium composed of a mixture of 50% of glucose and 50% of glycerol was used to seal the lid to the box opening. This mixture was insoluble in carbon disulphide, had no action on the sulphur, and its viscosity was such as to allow the lid to slide from the opening when the box was inclined.

To place this small charged calorimeter in position, the top portion of the copper jacket, *B*, Fig. 1, was removed and the calorimeter lowered in. One of the calorimeter axles ends in a small threaded bolt; this bolt screws into the end of a long axle connecting the calorimeter to a motor outside the bath.

The heat capacity of the small inner Stabrite steel calorimeter was carefully determined by measuring the temperature drop when weighed amounts of sodium chloride were dissolved within the calorimeter in weighed amounts of water. From the accurately known value of the heat of solution of sodium chloride in water and from this measured temperature drop, the heat capacity of the calorimeter was obtained with an accuracy of 0.3%.

The sulphur used in the research was Schuchardt's c. p. grade. It was dissolved in pure carbon disulphide and filtered twice through previously extracted filter papers, in order to obtain a perfectly clear solution of sulphur in carbon disulphide. From this solution the rhombic sulphur was recrystallized. In order to remove the last traces of carbon disulphide, the sulphur crystals were broken to the size of pin heads and heated for 24 hr. in an oven kept at 65° C. The purified sulphur was kept in a dark bottle away from light.

The carbon disulphide was a freshly obtained lot of Merck's c.p. grade. To ensure a high degree of purity it was redistilled from ceresine wax after the method of McKelvey and Simpson. The density of this purified carbon disulphide at 25.00° C. was found to be 1.2558 gm. per cc., as compared with 1.2556 gm. per cc. measured by the International Bureau of Physical Chemical Standards as the density of pure carbon disulphide.

Using this pure sulphur and carbon disulphide in the adiabatic calorimeter, the values shown in Table I for the heats of solution of rhombic sulphur in carbon disulphide were measured.

TABLE I

HEATS OF SOLUTION OF RHOMBIC SULPHUR IN CARBON DISULPHIDE

% Sulphur in solution	Heat of solution in calories per mole
Initial temp., 25° C.	
6.30	−405.3
6.30	−405.4
8.00	−404.4
11.73	−403.5
11.73	−403.4
14.19	−403.0
14.19	−403.2
16.56	−402.7
16.56	−402.5
Initial temp., 20° C.	
6.30	398.0
6.30	398.2
8.00	398.0
17.00	395.6
17.00	395.7

In calculating these results three small corrections were necessary. One arose from the cooling effect caused by the evaporation of carbon disulphide into the solute box as the solute box lid was removed, another in determining the heat effect caused by carbon disulphide vapor condensing in the calorimeter as the temperature of the calorimeter dropped owing to solution occurring, and a third was necessary in order to estimate the amount of heat developed due to rotation of the calorimeter. These corrections were all quite small, and in the most unfavorable cases could be summed with an accuracy that would not cause the final experimental result to be in error by more than 0.2%.

TABLE II

HEATS OF SOLUTION OF SULPHUR IN CARBON DISULPHIDE OBTAINED BY OTHER INVESTIGATORS

Observer	Temp., °C.	Concentration	Heat of solution, in cal. per mole
Bellati and Finazzi (2)	0	"Dilute"	−380.3
Bellati and Finazzi (2)	0	Concentrated	−369.6
A. Wigand (18)	0	6.43%	−386.9
A. Wigand (18)	0	8.41%	−396.3
A. Wigand (18)	0	8.74%	−389.2
S. U. Pickering (16)	20	Unstated	−470.4
M. Berthelot (4)	18	Unstated	−410±32

The foregoing results are represented graphically in Fig. 3, and they show that the heat of solution of sulphur in carbon disulphide changes only slightly with concentration and temperature. For purposes of comparison the results of previous investigators on the heat of solution of sulphur in carbon disulphide are given in Table II.

In regard to the accuracy of the values for the heats of solution measured by the authors, it is believed that, from an examination of the data entering into their calculation, they have an absolute accuracy of 0.5% and a relative accuracy of about 0.2%.

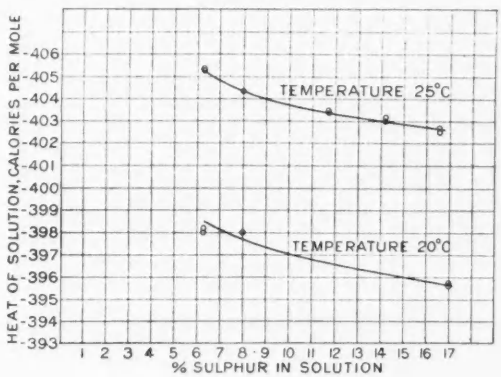

FIG. 3. *Heats of solution of sulphur in carbon disulphide at various concentrations.*

Specific Heat of Carbon-disulphide–Sulphur Solutions

The specific heats of carbon-disulphide–sulphur solutions entered into the calculation of the heats of solution when the total heat capacities of the calorimeter and contents were summed. The only values of specific heats available were those of Marignac, given in the International Critical Tables, and they are of unknown accuracy. It was found possible to calculate accurate values for the specific heat of carbon-disulphide–sulphur solutions by means of the relation

$$\frac{U_2 - U_1}{T_1 - T_2} = C_{Soln} - C_S - C_cS_2 ,$$

where U_2 = Heat of solution of sulphur at temperature T_2.
U_1 = Heat of solution of sulphur at temperature T_1.
C_{Soln} = Heat capacity of the solution.
C_S = Heat capacity of sulphur.
C_cS_2 = Heat capacity of carbon disulphide.

Values calculated for the specific heats of carbon-disulphide–sulphur solutions are shown in Table III.

TABLE III

SPECIFIC HEATS OF SULPHUR–CARBON-DISULPHIDE SOLUTIONS

% Sulphur in soln.	6.30	8.00	11.75	14.19	16.56
Sp. ht. of soln.	0.2373	0.2369	0.2361	0.2355	0.2349

The absolute accuracy of these values rests upon the value for the specific heat or heat capacity of carbon disulphide as used in the calculation. From the results of Regnault (17), Hirn (10), and Batelli (1), the specific heat of carbon disulphide was taken as 0.2389 cal. per gram at 22.5° C. The absolute accuracy of the foregoing specific heat values is probably within 1.0%, while the relative accuracy is within 0.1%.

Heat of Solution of Finely Divided Sulphur

Fine sulphur was prepared by grinding sulphur by means of a mechanically driven agate mortar and pestle. The sulphur was first ground to pass a 400 mesh screen. A preliminary heat of solution experiment was made with this 400 mesh sulphur, in order to discover whether there was a measurable quantity of surface energy associated with sulphur of this degree of fineness. The measurement showed that the heat of solution of this 400 mesh sulphur was 1.2 cal. positively greater than the heat of solution of the coarsely crystalline sulphur. In order to obtain a larger surface and a correspondingly larger surface energy, the 400 mesh sulphur was reground over a period of 12 hr. To insure that this very fine sulphur was not oxidized by the air, a quantity of it was allowed to remain in contact with the air of the laboratory for two weeks and then shaken with distilled water. A very dilute solution of potassium permanganate was added to this suspension of fine sulphur in water, and no decolorizing action was observed upon the potassium permanganate. This was taken to show that there was no solid and unstable suboxide of sulphur present in the finely divided sulphur. Solution of the finely divided sulphur in carbon disulphide also indicated that no amorphous sulphur had been formed in the process of grinding.

TABLE IV

HEATS OF SOLUTION OF FINELY DIVIDED SULPHUR

Temp., °C.	Conc'n of solution, %	Heat of soln., cal per mole
25.00	6.30	−401.2
25.00	6.30	−401.6
	Mean value	−401.4

With this finely divided sulphur the heat of solution measurements shown in Table IV were made.

This value for fine sulphur compares with the value of −405.3 cal. per mole for the heat of solution of coarse crystals of sulphur of the same solution concentration and at the same temperature. The difference between the heat of solution of fine, and that of coarse, particles is 3.9 cal. per mole. This value represents the difference between the total surface energy of coarse crystals and that of very fine crystals of sulphur.

Measurement of Particle Size

For the purpose of estimating the surface energy of solid sulphur per unit area, it was necessary to measure the average particle size of the finely divided sulphur. This was done by taking photomicrographs of the sulphur particles

scattered over glass plates. Under the microscope it was seen that the fine particles of sulphur had a marked tendency to cling together. This caused some difficulty in obtaining a clear picture of each individual particle. To scatter and separate the particles, a camel's-hair brush was filled with the fine sulphur and flicked beneath the glass plate, which was held in a gently rising current of air such as occurs near a warm electric light bulb. In another method used to separate the particles, a drop of glycoline was placed on a glass plate and a small amount of fine sulphur introduced into the drop. The drop was smeared over the surface of the glass plate to form a thin film, and photomicrographs were taken of the sulphur particles suspended in this thin layer of glycoline. A Bausch and Lomb metallographic microscope was employed for the work, and two magnifications of 200 and 500 diameters were used. A Brinnel microscope which superimposed an accurate scale graduated in tenths of a millimetre was found useful in reading the particle size from the photomicrographs.

The average diameter of the sulphur particles placed on the glass plate by scattering with a camel's-hair brush was found to be 5μ and 10μ for two different plates. However, even with this procedure, uncertainty arose in differentiating between single particles and aggregates.

The average diameter of the sulphur particle suspended in the layer of glycoline was found to be 5.9μ, 6.1μ and 6.8μ for three different plates in which dispersion was complete. Owing to the better concordance in these latter results their average was taken as the average diameter of the sulphur particle. The diameter of the average particle was calculated using the formula

$$D = \frac{(ad_1^3 + bd_2^3 + cd_3^3 \ldots\ldots)}{ad_1^2 + bd_2^2 + cd_3^2 + \ldots)},$$

where D is the diameter of the "average particle," defined as the diameter of the particle which, if wholly constituting the sulphur, would give the same area per mole as that of the actual particles It may be noted that this hypothetical diameter applies only to a hypothetical number of particles, but that the two may be used in conjunction to calculate correctly both area and volume. a is the number of particles of diameter d_1, b the number of particles of d_2, etc.

Assuming the particles to be spheres (as was indicated by the photomicrographs) and considering the particle diameter to be 6μ, the total surface energy of sulphur per square centimetre could now be calculated.

Area of surface per mole of 6μ sulphur = 160,000 sq. cm.

Surface energy per mole of 6μ sulphur = 3.9 cal.—$3.9 \times 4.2 \times 10^7$ ergs.

Total surface energy per sq. cm. $= \dfrac{3.9 \times 4.2 \times 10^7}{160{,}000} = 1024$ ergs.

The accuracy of this result for the surface energy of solid sulphur depends upon the value of 3.9 cal. as the difference between the heat of solution of fine sulphur and that of coarse sulphur, and upon the value of 6μ for particle

diameter. Owing to the great accuracy that can be obtained with the calorimeter when measuring heats of solution at a definite concentration, the value of 3.9 cal. would be correct to within 10%. There is greater uncertainty however regarding the value for the particle diameter. In the light of the facts that the screen opening was 38μ in diameter and that the sulphur was reground for 12 hr. after passing this screen opening, the value of 6μ would not appear too large. For these reasons it is considered that the value of the particle area is correct to within 30%. Based on this the value of 1024 ergs per sq. cm. for the total surface energy of solid sulphur should be accurate to within about 30%. Even within this accuracy it is of considerable interest to evaluate the surface energy of a non-metallic element such as sulphur.

The question of the influence of an adsorbed layer of gas on the value obtained for the surface energy of a solid is an open one. The authors favor the view that in the case of sulphur it is relatively small. However, experiments are to be carried out in which this factor will be further investigated.

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THE INFLUENCE OF HYDROGEN ION CONCENTRATION WITH PRETREATMENT OF WOOD ON ITS SUBSEQUENT DELIGNIFICATION[1]

By A. J. Corey[2] and O. Maass[3]

Abstract

The results obtained by the authors in a previous investigation have been checked. The influence of an acid, a salt and a base on the pretreatment of wood at 130° C. has been determined. It is shown that pretreatment of wood meal decreases the rate of subsequent delignification. Pretreatment was carried out over the temperature range 100° to 140° C. and the effect of temperature is shown to be very marked. As it was found that the pH of the water after pretreatment decreased, pretreatment was carried out on a chip in which the pH was kept more constant by a forced flow of water through the chip. It is shown that the rate of delignification is increased. Pretreatment was carried out in buffer solutions and it is shown that there is a pH value for which the influence of pretreatment is a minimum. The inferences drawn in connection with sulphite cooking are briefly discussed.

Introduction

In a recent paper (1) the pretreatment of spruce wood chips in water was described. It was found that the heating of the wood chips in water for several hours at 130° C. so changed the nature of the lignin in the wood that the rate of subsequent delignification by calcium bisulphite liquor was greatly retarded. This work has been repeated with a different wood specimen (black spruce). The results previously reported agree as closely as could be expected with the two different samples. The results of this last series are reported in Table I.

TABLE I

Effect of pretreatment of black spruce chips* on rate of delignification

Run no.	Yield of pulp, %	Yield of cellulose, %	Mullen strength, %	Lignin in pulp, %	Residual lignin, %	Length of cook, hr.
A. No pretreatment—cooked at 140° C.						
140	70.0	53.3	—	23.9	16.7	1
139	56.7	49.5	123	12.7	7.2	2
136	52.7	48.5	148	7.96	4.20	3
138	47.3	45.5	134	3.85	1.82	4
137	47.0	46.1	143	2.01	0.94	5
B. Preheated in water for 6 hr. at 130° C.—cooked at 140° C.						
145	74.7	56.6	—	23.1	17.2	1½
141	62.2	51.2	—	17.6	10.9	3
147	56.9	48.5	85	14.7	8.4	4
146	52.8	47.8	99	9.33	4.92	5
144	47.0	44.6	110	4.95	2.33	6
143	42.2	41.0	102	2.99	1.26	7
142	39.7	38.6	95	2.76	1.09	8

* *Density, 0.34; lignin content, 29.9%.*

[1] *Manuscript received September 18, 1935.*
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An investigation was then made to determine the effect due to the presence of acids, alkalies and salts in the pretreating solution. Wood samples, in the form of chips, were impregnated with water and then heated in various solutions for six hours at 130° C. The chips were removed from the solution and thoroughly washed to remove all traces of the reagent, then dried and cooked according to standard procedure. Two different wood specimens were used. The results of the runs are therefore tabulated in two parts, with a standard cook of each specimen for comparison.

TABLE II

EFFECT OF PRESENCE OF ACIDS, ALKALIES AND SALTS IN THE PRETREATING SOLUTION

Run no.	Yield of pulp, %	Yield of cellulose, %	Lignin in pulp, %	Residual lignin, %	Length of cook, %	Reagent
A. Density of wood, 0.33. Pretreated in neutral salt and alkaline solutions at 130° C. for 6 hr. and cooked at 140° C.						
110	53.2	49.3	7.35	3.9	3	No pretreatment
148	60.7	51.8	14.6	8.85	3	Sat'd. KCl soln.
151	71.3	58.6	17.9	12.7	4	Sat'd. $Ca(OH)_2$ soln.
120	67.5	54.0	20.0	13.6	3	Pretreated in H_2O
B. Density of wood, 0.34. Pretreated in acid and alkaline solutions at 130° C. for 6 hr. and cooked at 140° C.						
138	47.3	45.5	3.85	1.82	4	No pretreatment
149	59.8	51.2	14.4	8.62	4	N/10 acetic acid soln.
150	74.1	47.8	35.5	26.3	4	N/10 NH_4OH soln.

It is seen from Table II, A, that pretreatment of wood in a saturated potassium chloride solution at 130° C. has less effect on the rate of delignification than pretreatment in water. However the subsequent rate of delignification is only one-half that of untreated wood cooked under the same conditions. Heating wood in a saturated solution of calcium hydroxide has a very marked effect on the rate of delignification, as shown in Run 151, in which the time of cooking was one hour longer than that in the others, yet the residual lignin content was nearly as high as that in the pulp obtained in Run 120.

Comparing Run 149, Table II, B, with Run 147 in Table I, B, it is seen that pretreatment of wood in $N/10$ acetic acid solution has about the same effect as pretreatment in water under similar conditions. Pretreatment of wood in $N/10$ ammonium hydroxide solution makes the subsequent delignification extremely difficult, less than 4% of the lignin having been removed from the wood after four hours of cooking.

Since it was shown that the cooking properties of wood are affected by pretreatment in both acid and alkaline solutions, it seemed probable that the effect was due to the hydrogen ion concentration of the solution. When wood is heated in distilled water the solution becomes acidic, owing to the

formation of acetic and formic acids. Thus the pretreatment of wood in water really consists of heating wood in an acid solution. In order to determine whether wood structure was an important factor in the pretreatment phenomenon, two samples of wood meal were cooked four hours in bronze bombs of 200 cc. capacity. One sample had been previously heated in water for five hours at 130° C., while the other was untreated. Although the effect was not as striking as that obtained with chips, yet a definite decrease in the rate of delignification was noted in the case of the pretreated wood meal.

TABLE III

THE EFFECT OF PRETREATMENT IN WATER ON WOOD MEAL

Run no.	Yield of pulp, %	Lignin in pulp, %	Residual lignin, %	Condition of wood meal
156A	52.0	4.57	2.37	Pretreated in water
156B	41.8	1.59	.66	Untreated

It is evident that the higher the temperature employed in the pretreatment, the greater will be the quantity of acid formed in the solution. The following series of cooks were made to determine the relation between temperature of pretreatment and the decrease in the rate of delignification. Since the acidity of the solution depends on the temperature, this series also gave an indication of the relation between decreased rate of delignification and the pH of the pretreating solution.

Samples of wood were pretreated in water at 100°, 110°, 120°, 140° C. for six hours, after which they were cooked for three hours at 140° C. pH determinations were made on the cold solutions obtained after the pretreatment.

TABLE IV

WOOD PRETREATED IN WATER AT VARIOUS TEMPERATURES, AND COOKED THREE HOURS AT 140° C.

Run no.	Yield of pulp, %	Yield of cellulose, %	Lignin in pulp, %	Residual lignin, %	Temp. of pretreatment, ° C.	pH of solution
136	52.7	48.5	7.96	4.20	No pretreatment	—
162	48.0	43.5	9.57	4.59	100	4.45
165	53.4	49.1	8.08	4.32	110	4.55
164	58.3	50.1	14.2	8.27	120	4.25
141	62.2	51.2	17.6	10.9	130	—
163	61.2	41.8	31.6	19.4	140	3.42

These results show that there is a close relation between the residual lignin and the pH of the pretreating solution, but they also suggest that the temperature is a very important factor, since only a narrow range of pH has been covered, yet at high temperatures the effect becomes very pronounced. It is well to emphasize here that all pH determinations reported in this paper

were made on solutions at room temperature, and thus give only relative values at a higher temperature. Also, when wood is heated in water, the acid is formed within the wood chip and, owing to slow diffusion, the wood is subjected to a higher acidity than an investigation of the solution would indicate. This is clearly shown in the following series of cooks, in which an attempt was made to pretreat wood in a neutral solution. This necessitated the removal of the acid, formed in the chip, at such a rate that the acidity would always be negligible.

In Run 166 the wood chips were placed in the small cooking cell of the penetration apparatus (2, p. 10), and during pretreatment a constant flow of distilled water, about 10 cc. per min., was maintained.

A second attempt consisted of pretreating wood chips in a solution buffered to a pH of 7. McIlvaine's standard buffer solutions were used (3). The pretreatment in Run 169 was carried out in the penetration cell developed in this laboratory (2, p. 9). A cylinder of wood 3½ cm. in diameter and 2 cm. in length was clamped in the cell, and during the pretreatment distilled water was forced under pressure through the chip. The rate of flow was about 10 cc. per min. The centre portion of this chip was used for the cooking experiment, and the results are compared with a run made on the same wood but without pretreatment. The pretreatment in each case consisted in heating the wood in the specified solution for six hours at 130° C., and the wood was then cooked three hours at 140° C.

TABLE V

A COMPARISON OF COOKS MADE UNDER VARIOUS CONDITIONS OF PRETREATMENT

Run no.	Yield of pulp, %	Yield of cellulose, %	Lignin in pulp, %	Residual lignin, %	Conditions of pretreatment
136	52.7	48.5	7.96	4.20	No pretreatment
141	62.2	51.2	17.6	10.9	Heated in water for 6 hr. at 130° C.
166	56.0	48.8	12.9	7.23	Flow of distilled water during pretreatment
168	65.4	56.2	14.01	9.2	Solution buffered to a pH of 7
169	50.3	48.2	4.16	2.09	Forced penetration of distilled water through the chip
6	53.0	51.3	3.32	1.76	No pretreatment

The pretreatment used in Run 166 had little effect on the rate of delignification, compared with normal pretreatment in water, as shown by Run 141. There is an appreciable difference between it and no pretreatment (Run 136). That is easily understood since, although the solution around the chips was changed, the diffusion factor is so great that a marked effect is still obtained. The results of later work, reported in this paper, will explain the significance of Run 168. Run 6 was made under a temperature schedule which differed from that of Run 169 only in that it would correspond to a slightly longer cooking time, so the results are considered to compare fairly closely.

During the pretreatment in Run 169 there must have existed a concentration gradient within the chip, and, since the distilled water used had a pH of about 5.7, the chip must have been heated in the presence of a solution of pH about 4 to 5 as measured at room temperature. This assumption is borne out by later work.

For the next two series of cooks white spruce woodmeal was used. The density was 0.39 and the lignin content 30.9%.

Six samples were sealed in glass bombs filled with buffer solutions of pH ranging from 3 to 8, and heated at 130° C. for six hours. They were then cooked in bronze bombs for three hours at 140° C. The results are tabulated in Table VI, and the curves of lignin in the pulp *versus* pH, and yield of pulp *versus* pH, are shown in Fig. 1.

Series 173 shows the rate of removal of the lignin for a given pH of the pretreating solution. Three samples of woodmeal were pretreated in solutions buffered to a pH of

TABLE VI

SERIES 172. WOODMEAL PRETREATED AT 130° C. FOR SIX HOURS IN SOLUTIONS OF pH 3–8

pH of solution	Yield of pulp, %	Lignin in pulp, %	Residual lignin, %
3	56.0	10.4	5.83
4	53.0	7.4	3.93
5	52.5	7.25	3.81
6	56.0	8.37	4.78
7	58.8	12.6	7.40
8	62.6	14.2	8.89

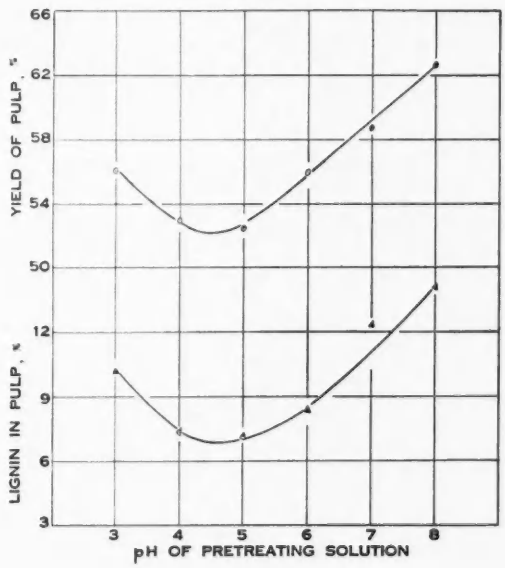

FIG. 1

3, and three in solutions buffered to pH 7. The pretreatment was carried out in glass lined bronze bombs to prevent contamination of the product through the reaction of the solution on the bronze. After periods of two, four and eight hours a bomb from each set was removed. The temperature was maintained at 130° C. After suitable washing and drying the samples were cooked in the glass lined bombs for three hours at 140° C.

Discussion

When the yields of pulp and the lignin in the pulp in Series 172 are plotted against the pH of the pretreating solutions, a minimum is obtained corresponding to a pH between 4 and 5 (Fig. 1) determined on the cold solution. On either side of this minimum the curve rises rapidly, thus explaining the results obtained in Run 168.

From the results of Table VII (Fig. 2) it is seen that for pH below and above 4.6 the length of time of pretreatment increases the difficulty of delignification. At pH 3 the influence of time of heating is as might be expected, approaching a constant value. At pH 7, increased time of pretreatment seems to have an accelerating influence on the difficulty of subsequent delignification. This accounts for the extraordinary influence of ammonia in the pretreating solution.

TABLE VII

SERIES 173. WOODMEAL PRETREATED AT 130° C. FOR TWO, FOUR AND EIGHT HOURS IN SOLUTIONS OF pH 3 AND pH 7

pH of solution	Length of pretreatment, hr.	Yield of pulp, %	Lignin in pulp, %
3	2	47.2	5.3
3	4	53.8	12.7
3	8	58.7	17.2
7	2	54.7	8.46
7	4	55.6	10.8
7	8	63.0	19.2

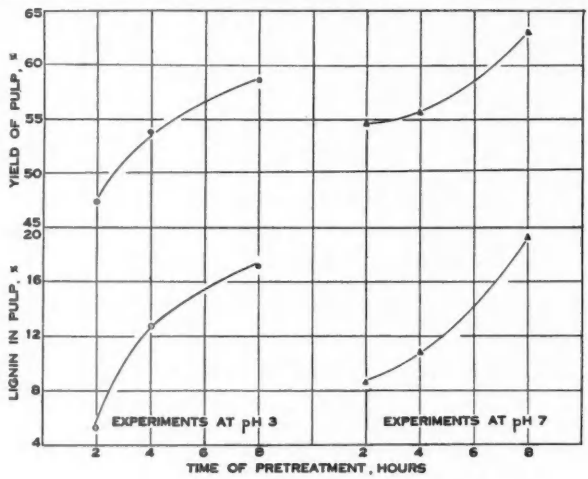

FIG. 2

It cannot be predicted at present in what manner the pH of the buffer solutions will alter with temperature*, but from Fig. 1 it is evident that at a definite hydrogen ion concentration wood may be heated at 130° C. for as long as six hours without any appreciable change in its subsequent cooking properties. Heating the wood in a solution of a higher or lower concentration of hydrogen ion changes it in such a way that it becomes very difficult to delignify by the sulphite process. This is in agreement with the experiment of Klason (4) on the pretreatment of wood meal with hydrogen ion concentration corresponding to a pH of over 7, which greatly retarded subsequent delignification.

The foregoing results are of particular interest in connection with the delignification of wood by sulphite liquor. Work by Gishler and Maass shows that the pH of sulphite liquor at the start of the cook is of the order 3 over a considerable range of concentration, this value being determined at the temperature of the cook. This is lower than the optimum pH that would be deduced from the experiments cited above, and once cooking starts the pH is still further lowered by the formation of sulphonic acids. As was stated above, the optimum pH of 4.6 is that of the buffer solution measured at room temperature, and may in reality be lower. If on further investigation it is found that the optimum pH does not coincide with that of sulphite liquor, it will follow that reduction in cooking time by methods of penetration will be of advantage.

From the results obtained so far it is impossible to deduce with certainty what the influence of hydrogen ion concentration is on the solubilization of lignin, that is, whether a chemical or colloidal change, or a combination of both, takes place. Investigation to clear up this point is under way.

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** The pH of the solutions used for pretreatment were tested before and after, and it was found that the pH as measured at room temperature was unaltered. The alteration referred to means that, although the pH at 25° C. can be measured at room temperature, there is no telling what it will be at 130° C.*

THE DISCONTINUITY IN THE DIELECTRIC CONSTANT OF LIQUIDS AND THEIR SATURATED VAPORS AT THE CRITICAL TEMPERATURE[1]

By J. Marsden[2] and O. Maass[3]

Abstract

A dielectric cell, which is specially adapted to a study of the dielectric constants of liquid and gas over a large temperature range, including the critical temperature region, is described. The dielectric constants of methyl ether (liquid and saturated vapor) and propylene (liquid and saturated vapor), from room temperature to eight degrees above the critical temperatures, are given. The measurements show that the dielectric constants of liquid and gas are not identical at the critical temperature. These results are in agreement with previous work carried out in this laboratory on the discontinuity in properties of the medium above and below the point of disappearance of the meniscus.

Introduction

In 1902 Eversheim (3, 4) measured the dielectric constant of hydrogen sulphide, liquid and saturated vapor, over a temperature range that extended above the critical temperature of this substance. The data from this research, together with those obtained in its subsequent investigation in 1904, are included in the International Critical Tables (5). Their method of presentation, however, has been altered. Whereas Eversheim plotted his curves in such a way as to indicate that the difference between the dielectric constant of liquid and that of the gas persisted above the critical temperature, care has been taken in the compilation of these data in the International Critical Tables to draw in a curve conforming to the classical idea, that at the critical temperature (disappearance of a visible meniscus) the properties of liquid and saturated vapor become identical.

Experiments in this laboratory (2, 11, 12, 13) have indicated that when a pure liquid is heated somewhat above the critical temperature, even with prolonged stirring, such is not the case.

The actual experimental results of Eversheim seem to be in agreement with the latter point of view. In his later experiments he found that when the condenser was shaken the difference became less marked. It seems difficult to explain why the dielectric constant of the liquid at room temperature should be different, when the liquid was shaken and when it was not shaken, so that it seems possible that the shaking introduced some influence on the measurement of capacity. When the actual experimental results obtained by Eversheim, when the condenser was shaken, are plotted, there is still a marked difference between the dielectric constants above and below the critical temperature.

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More recently Litvinoff and Litvinoff (7) measured the dielectric constant of liquid ethyl ether over a temperature range including the critical temperature, and found that the dielectric constant of the liquid decreased from a value of 1.796 at 194° C. (critical temperature) to a value of 1.760 at 200° C.

The work in this laboratory showed that if a difference in property existed between the medium above and below the disappearing meniscus, such a difference persisted, provided that there was no measurable temperature difference between top and bottom of the thermostat. Consequently, it was decided to investigate the dielectric constant of propylene and methyl ether, both for liquid and saturated vapor, paying special attention to this precaution.

The pioneer work in this direction was carried out by H. E. Morris (10) in this laboratory. Unfortunately, the repeated failure of the glass, with platinum sealed contacts, prevented the completion of this work. However, results were obtained for propylene, up to within a few degrees of the critical temperature which indicated that an extrapolation of the experimental results would show a marked discontinuity between liquid and saturated vapor at the critical temperature.

The main object of this study was then to investigate the possible persistence of the properties of a liquid above the critical temperature.

Reference to other investigators has been made in previous papers published by this laboratory (2, 11, 12, 13), and there will also be found a discussion regarding their significance.

On account of the unusual experimental difficulties involved, few data are available on the dielectric constant of liquid and saturated vapor, over a temperature range including the critical temperature. At the critical temperature, the dielectric constants of most substances are small, and the pressures involved are very large. Small capacities have therefore to be used.

Experimental

The Dielectric Cell

The first requirement in this investigation was a cell made of glass, in order that the behavior of the meniscus might be observed. This necessitated an electrical contact, made through some type of a glass-metal seal capable of standing pressures as high as 60 atm. Morris (10) found that platinum-glass seals did not withstand the pressures encountered. This difficulty was overcome by the use of frozen mercury seals.

The apparatus is shown diagrammatically in Fig. 1. The condenser bomb, *G*, of specially annealed Pyrex glass, with an internal diameter of 16 mm. and thickness 4–5 mm., was connected by means of capillary tubing to the counterpoise bomb, *H*, of an internal diameter of 13 mm. and thickness 2–3 mm. The condenser, *A*, consisted of a series of concentric brass cylinders, insulated by glass rods and fastened together, so that it could be moved as a unit. The capacity of the condenser was approximately 25 $\mu\mu f$.

The condenser was connected to a soft iron counterpoise, *E*, by means of a fine brass wire which served also as a lead for the outer plates of the condenser. Copper wire insulated with cotton was soldered to the lead wire, and passed longitudinally through the centre of the counterpoise, and was soldered in turn to a brass spring, *B*. Another spring, fastened to the bottom of the condenser, served as a lead for the outer plates of the condenser. The springs were sufficiently flexible to permit an unhampered movement of the condenser. The end of each spring was soldered to a nickel wire which made contact with the mercury. The wires were in turn wedged into place in the capillary, so that the springs were kept taut.

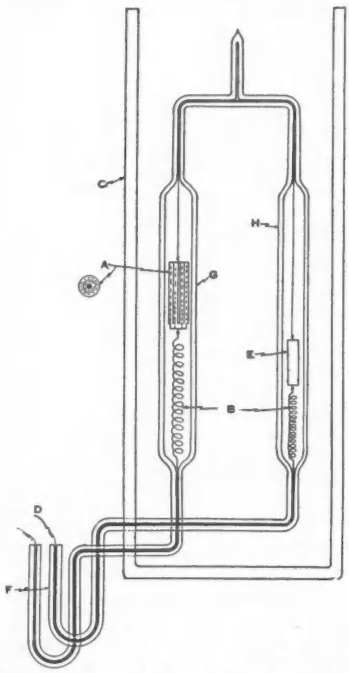

FIG. 1. *Diagram showing the dielectric cell.*

The capillary arms of the cell passed through two holes drilled in the side of a Pyrex jar *C*, where they were fastened securely with litharge-glycerine cement, and each terminated in the form of a U. Mercury was introduced into these U-tubes and frozen with a carbon-dioxide–acetone mixture. Hydrochloric acid was added to the latter, to make it a conducting medium, which could be grounded. Care had to be taken that no air was trapped by the mercury, otherwise on evacuation it would be drawn up into the cell. To prevent this, the mercury seals were filled simultaneously by means of a T-joint connecting the U-tubes to a manometer provided with an attached leveling bulb. After evacuation of the cell, the leveling bulb was raised until the desired amount of mercury was introduced.

Contact between the measuring set up and the dielectric cell was made through two wires, *D*, dipping into the mercury seals.

Measurement of Dielectric Constant

The heterodyne beat method was used for measuring capacity. In the preliminary work carried on by Morris (10), the oscillators were of the Hartley type. This apparatus had one serious disadvantage in that it was affected by stray capacities. This difficulty may be overcome by special operating technique when the experimental cell is placed near the measuring apparatus.

However, in this work the experimental cell had to be placed about eight feet from the measuring apparatus. Stray capacities were also introduced by the metal supports surrounding the bath.

The measuring apparatus finally adopted by Morris (10) and used by the authors is shown in Fig. 2. The Hartley principle was replaced by a tuned plate circuit in which the plates of the variable condensers were grounded;

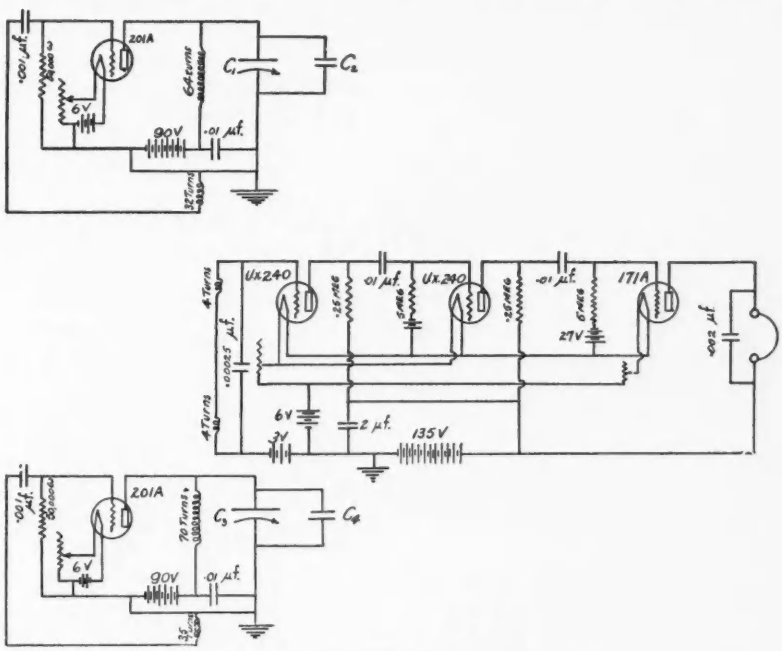

FIG. 2. *Diagram showing oscillators and amplifier.*

body capacities were thus eliminated. The hook-up consists of two oscillators with a detector and amplification unit. A frequency of 1,000,000 was employed.

Since small changes in capacity were measured, the following method of increasing the accuracy of the readings was used. A mirror, with a vertical cross hair was fastened to the arch of the rotor plates of the condenser. The latter was placed in the centre of a five foot wooden circle, with a vertical millimetre scale around its circumference. A beam of light directed on the mirror and reflected to the scale gave a sharp shadow of the cross hair capable of being read to 0.5 mm. The condenser was adjusted, by means of a pulley attached to the rotor plates, and connected to another pulley placed outside the wooden circle.

The experimental condenser C_2 was placed in parallel with C_1, and could be cut out by means of a mercury switch, thus allowing the lead capacities to be checked after every reading. This switch, placed near the experimental cell, was operated by a system of pulleys at a safe distance from the bath. The oscillators and amplifier were enclosed in galvanized iron boxes. All leads were encased in copper tubing and the latter grounded. A condenser, C_4, was inserted to offset lead capacity.

In operation, the variable condenser, C_3, was adjusted so that a zero sound reading was obtained when the condenser C_1 was set in a position such that it gave a convenient reading on the scale. The experimental cell C_2 was connected in parallel with C_3 and C_1 readjusted. The difference in capacity of C_1 gives the capacity of C_2. The set-up was such as to make the range of inaudibility in the phones small, and the difference between the scale reading at which sound could be heard and that at which it could not be heard was less than 2 mm. In making measurements the zero sound reading was, of course, always approached from the same direction. A change of 0.00192 in dielectric constant corresponded to a change of 1 mm. on the scale. For each dielectric constant determination, the reading for the leads and that for the cell inserted were taken, and the reading for the leads checked. This series of observations was repeated four times at about two-minute intervals. It was found that the scale readings agreed within 1 mm. on the average. The procedure for the calculation of dielectric constant will be shown later.

The Heating Bath

The bath, C (Fig. 1), was a three gallon Pyrex jar. Dibutyl phthalate was used as the liquid medium since it does not discolor as rapidly as most bath liquids. It was thus possible to see the meniscus in the bomb.

A steel drum which served the double purpose of a shield for the experimental condenser, and also as a preventive measure in case of an explosion, surrounded the thermostat. Three 200-watt Mazda lamps placed behind holes cut in the drum gave suitable lighting in the thermostat.

The dielectric cell was supported by two adjustable aluminium rings, attached to a steel rod.

Vertical movement of the condenser was effected by means of a solenoid, with an iron core, which controlled the position of the counterpoise. This solenoid was mounted on a carrier running in a grooved brass rod. The carrier was connected by a steel chain which passed over a toothed wheel, mounted on an axle, to a lead counterpoise. A large pulley fixed on this axle and connected by a belt to another pulley about eight feet distant, permitted manipulation of the magnet at a safe distance from the bath.

In a study of this kind, one of the most important factors is temperature control. Not only must the temperature be kept constant, but also a temperature gradient, between top and bottom of the bomb, must be avoided. By means of a telescope, temperatures were read on a standardized thermometer graduated in tenths of a degree. A copper-constantan thermo-

couple, having four junctions at the bottom and four junctions at the top of the bomb, indicated any temperature difference. The thermocouple was connected to a sensitive D'Arsonval galvanometer. A scale was placed about seven feet from the mirror of the galvanometer. A deflection of 1 cm. on this scale corresponded to a temperature differential of 0.02° C.

Two heaters were placed at the sides of the bath, and one at the top and one at the bottom; the last two were so adjusted as to eliminate any temperature difference shown by the thermocouple. A four bladed stirrer was used. It was found possible to maintain uniformity of temperature in the bath to better than 0.01° C.

A 110 volt d.c. circuit supplying power for heaters, magnet and motor was grounded through a 10,000 ohm resistance. All metal parts surrounding the bath were grounded.

The whole bath assembly was enclosed in a wooden box fitted with safety glass windows.

Preparation for an Experiment

The capillary T-joint at the top of the dielectric cell was connected to a vacuum pump. The cell was heated to 100° C. and alternately evacuated and flushed with air dried over phosphorus pentoxide.

Propylene was prepared, as described by Maass and co-workers (1, 8, 9), by the dehydration of isopropyl alcohol over alumina at 350° C. Purification was carried out by low temperature fractionation, the purity being checked by the vapor pressure after every fractionation.

Methyl ether (99.9%), obtained from Ohio Chemicals, Ltd., was condensed into the fractionation system, and purified in the manner described for propylene.

The cell was evacuated and flushed several times with the substance to be investigated. A volume of liquid equal to 24/85 of the total volume of the cell was distilled in, from a graduated tube, the bath being cooled with a carbon-dioxide–acetone mixture.

C. p. benzene, dried over sodium, was used in the calibration of the condenser.

Results

*Methyl Ether**

The condenser was calibrated with air and benzene. The dielectric constant of liquid methyl ether at two temperatures was then calculated from these data, the temperatures chosen being such that the dielectric constants differed by a large amount. These measurements were made directly, one after the other. Knowing the dielectric constant at these two temperatures, these values could be used in all subsequent experiments for purposes of calibration. This was necessary in view of the fact that there was a slight change in the capacity of the set-up, owing to the rearrangement of the apparatus and to other causes. The foregoing calibration was carried out as follows.

* *Critical temperature, 126.9° C.*

The dielectric constant of the medium in the condenser cell is C_x, where C_x is the capacity when the medium is substance x and C_a when it is air.

Let C_b = capacity of condenser in benzene
C_m = capacity of condenser in methyl ether
ϵ_b = dielectric constant of benzene
ϵ_m = dielectric constant of methyl ether.

Then

$$C_b = \epsilon_b C_a \tag{1}$$
$$C_m = \epsilon_m C_a . \tag{2}$$

The capacity of the condenser in air is given by

$$L + C_a = kD_a, \tag{3}$$

where L is the capacity of the internal leads, including mercury seals, D_a is the deflection of the experimental condenser in air, as measured on the scale of the precision condenser, and k is the proportionality factor. Similarly

$$L + C_b = kD_b \tag{4}$$
$$L + C_m = kD_m . \tag{5}$$

It follows, by substituting the values of C_b and C_m obtained by means of Equations (1) and (2) in Equations (4) and (5), respectively, that Equations (3), (4) and (5) may be solved simultaneously to give

$$\epsilon_m = \left\{\frac{(D_m - D_a)(\epsilon_b - 1)}{(D_b - D_a)}\right\} + 1.$$

From this equation the dielectric constant of methyl ether was determined at two temperatures, t_1 and t_2, the deflections being D_{t_1} and D_{t_2}.

From previous equations it follows that,

$$C_a(\epsilon_{t_1} - 1) = k(D_{t_1} - D_a)$$

and

$$C_a(\epsilon_{t_2} - 1) = k(D_{t_2} - D_a).$$

Solving

$$k = \frac{C_a(\epsilon_{t_1} - \epsilon_{t_2})}{(D_{t_1} - D_{t_2})}.$$

TABLE I

THE RELATION BETWEEN THE DIELECTRIC CONSTANT OF LIQUID METHYL ETHER AND TEMPERATURE

Temp., °C.	Dielectric constant	Temp., °C.	Dielectric constant	Temp., °C.	Dielectric constant
24.5	5.034	95.8	3.338	127.6	1.903
37.3	4.732	100.3	3.227	128.2	1.899
50.5	4.424	103.2	3.167	128.3	1.885
55.5	4.310	104.9	3.114	130.4	1.878
60.6	4.179	109.0	2.993	131.7	1.873
66.3	4.048	115.3	2.811	135.6	1.860
69.95	3.949	116.9	2.749		
75.0	3.831	120.6	2.615	*Hysteresis curve*	
80.3	3.712	123.2	2.492		
85.1	3.598	125.0	2.369	130.0	1.874
90.2	3.474	126.1	2.257	127.8	1.882

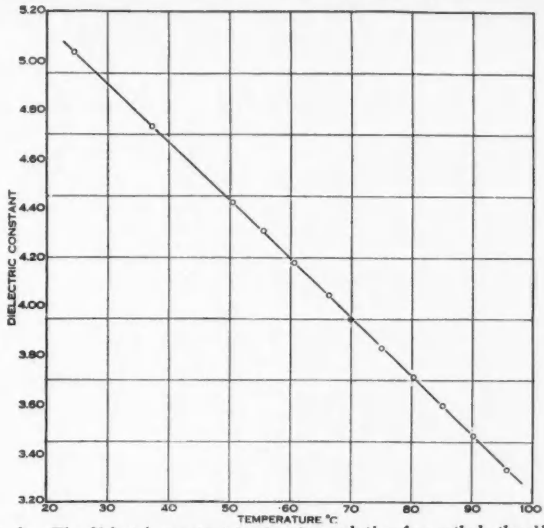

FIG. 3. *The dielectric constant-temperature relation for methyl ether liquid from 25° to 100° C.*

Having determined $k(0.0193C_a)$, it was possible to calculate the dielectric constant of methyl ether at any other temperature at which the deflection was measured.

It was convenient to obtain the dielectric constant of the gas above the critical temperature by raising the condenser into the gas phase, and comparing the dielectric constant of the gas with that of the liquid. The reason for this will be discussed later. The dielectric constant of the gas was calculated on the assumption that the dielectric constant of the liquid and that of gas were the same at 135° C., eight degrees above the critical temperature, *i.e.*, 1.860 as determined from the liquid curve. Knowing the change in deflection of the condenser with change in temperature and the dielectric constant at 135° C., the dielectric constant was determined for different temperatures, in the same manner as described for the liquid.

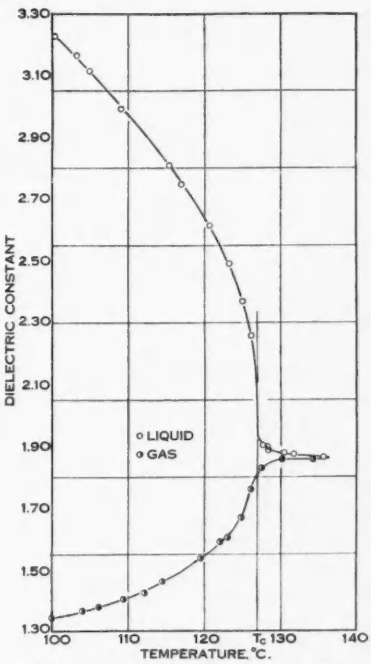

FIG. 4. *The dielectric constant-temperature relation for methyl ether liquid and gas from 100° to 135° C.*

TABLE II

THE RELATION BETWEEN THE DIELECTRIC CONSTANT OF METHYL ETHER GAS AND TEMPERATURE

Temp., °C.	Dielectric constant	Temp., °C.	Dielectric constant	Temp., °C.	Dielectric constant
59.2	1.225	112.2	1.426	126.0	1.760
80.0	1.262	114.5	1.462	127.4	1.827
100.0	1.343	119.5	1.538	130.1	1.858
104.1	1.364	122.0	1.590	134.1	1.856
106.1	1.377	123.0	1.605		
109.4	1.404	124.8	1.667		

*Propylene**

The dielectric constants of propylene were calculated from the absolute values of the dielectric constant at 45 and 65° C., as given by Morris (10). The relative changes in deflection with temperature were measured, and the dielectric constants calculated in the same way as described for methyl ether. The value of the proportionality constant, k, is 0.0191 C_a. Incidentally, this is an independent check of the value 0.0193 C_a found in the previous calibration.

TABLE III

RELATION BETWEEN THE DIELECTRIC CONSTANT OF PROPYLENE LIQUID AND TEMPERATURE

Temp., °C.	Dielectric constant	Temp., °C.	Dielectric constant	Temp., °C.	Dielectric constant
21.0	1.873	65.0	1.690	89.9	1.445
25.1	1.864	67.9	1.669	90.7	1.419
29.9	1.852	71.4	1.654	91.4	1.375
34.5	1.843	75.7	1.625	91.6	1.350
39.2	1.824	81.1	1.579	91.9	1.331
45.0	1.795	83.5	1.547	93.1	1.318
50.2	1.779	87.6	1.493	96.4	1.314
54.8	1.742				

The dielectric constant of the gas was calculated in the same way as described for methyl ether. The dielectric constant of gas and liquid were assumed to be equal at 100° C., eight degrees above the critical temperature.

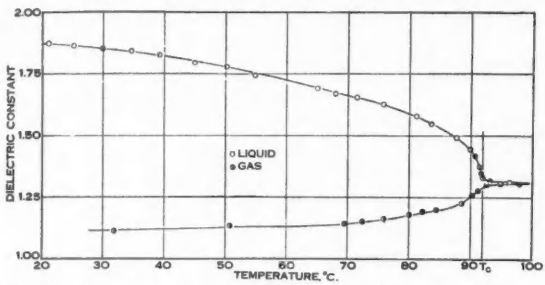

FIG. 5. *The dielectric constant-temperature relation for propylene liquid and gas.*

* *Critical temperature, 91.9° C.*

TABLE IV

RELATION BETWEEN THE DIELECTRIC CONSTANT OF PROPYLENE GAS AND TEMPERATURE

Temp., °C.	Dielectric constant	Temp., °C.	Dielectric constant	Temp., °C.	Dielectric constant
31.8	1.114	80.0	1.182	90.2	1.258
50.8	1.134	82.2	1.194	91.1	1.279
69.5	1.144	84.4	1.203	92.6	1.304
72.4	1.151	88.5	1.228	94.8	1.310
75.9	1.165	89.9	1.254	98.0	1.310

Discussion

The cell has been designed in such a way that simultaneous measurements of the dielectric constants of liquid and vapor could be made by moving the condenser, by means of the magnet. This was, of course, of particular interest in connection with determinations above the critical temperature.

Such experiments were carried out with propylene and the results shown in Table V were obtained.

TABLE V

DIELECTRIC CONSTANTS OF PROPYLENE GAS AND LIQUID* (NOT CORRECTED FOR DISPLACEMENT OF CONDENSER)

Temp., ° C.	°C. above critical	ϵ liquid	ϵ gas
91.9	0	1.331	1.226
93.1	1.2	1.318	1.239
96.4	4.5	1.314	1.257

** As determined by simultaneous measurements on liquid and gas, above the critical temperature. The constants for the gas are based on the absolute values of the liquid, with the assumption that displacement of the condenser cell from its normal position in the liquid caused no change in capacity.*

It will be seen that with rise in temperature the dielectric constants of gas and liquid approach each other, but the difference is far too great when compared with the results of Winkler and Maass (13), and Tapp, Steacie and Maass (12).

It was thought that this might be due to a change in capacity when the condenser system is moved vertically in a uniform medium. This could be accounted for by a relative change in position of the brass spirals during the movement. Consequently measurements were carried out when the condenser arm was filled with benzene. It was found that there was a change in capacity.

This change in capacity can best be presented in terms of an apparent change in the dielectric constant of benzene, for purposes of the calculation of the dielectric constant of the gas. When the condenser was immersed in the liquid propylene (the normal position in the liquid), the accepted value for the dielectric constant of benzene at 59.2° C. of 2.198 is taken (6). When the condenser was moved into the position where, in the propylene medium it was in the gas (normal position in the gas), the apparent dielectric constant of benzene was found to be 2.145. These changes in capacity were found to be

reproducible, thus showing definitely that there was a change in capacity when the position of the condenser was changed in the condenser arm filled with a uniform medium, the counterpoise arm being filled with air.

When this correction is applied to the results shown in Table V, the values of the dielectric constant shown in Table VI are obtained.

TABLE VI

DIELECTRIC CONSTANTS OF PROPYLENE GAS AND LIQUID* (CORRECTED FOR DISPLACEMENT OF CONDENSER)

Temp., °C.	ϵ liquid	ϵ gas
91.9	1.331	1.279
93.1	1.318	1.292
96.4	1.314	1.310

** As determined by simultaneous measurements of liquid and gas above the critical temperature. The constants for the gas are based on the absolute constants of the liquid, but are corrected for the displacement of the condenser ceil, the corrections being based on the apparent variation of the dielectric constant of benzene with displacement from the normal position.*

It was decided not to use this method, as the correction is probably not quite sound. This is because of the fact that the medium (propylene or methyl ether) introduced into the cell was of such an amount that some liquid was in the counterpoise arm, since as it has to be arranged that the visible meniscus in the condenser arm would disappear in such a position that the condenser could be moved from below to above the point of disappearance of the meniscus*.

However, these data illustrated the following phenomenon. When the meniscus disappears, a difference in medium persists above and below the point where it was last seen. This difference becomes less with rise in temperature, above the critical. As the bath temperature was kept constant, at each temperature above the critical, during the time when the condenser was moved up and down, these experiments show that the considerable stirring brought about by this movement did not destroy the difference in dielectric constant.

Because of the uncertainty of the correction to be applied for the up and down movement of the condenser, the absolute values for the dielectric constants of the gas were calculated on the assumption that at 8° C. above the critical temperature the medium would be uniform, within the accuracy of measurement.

The data presented are of interest in two ways. The dielectric constant of two liquids and their saturated vapor have been measured, and it has been shown that above the critical temperature a difference in dielectric constant persists between the medium, above and below the disappearing meniscus.

The interest attached to the first will be discussed in a subsequent paper, as it was not the main object of the present investigation, except in so far as

** It was mentioned before that the space was filled to 24/85 of the total volume of the bomb, in order to have the meniscus disappear at the same position, as it was at room temperature. This was very difficult on account of the large dead space in the counterpoise arm, as well as in the condenser arm. The distribution of liquid between the condenser arm and counterpoise arm was brought about by evaporation and condensation, and by trial and error the relative amounts were so adjusted that the condition mentioned above could be brought about.*

to point out the extraordinary difference in the shapes of the methyl ether and the propylene curves (Figs. 4 and 5). The dielectric constant of liquid methyl ether decreases with extraordinary rapidity from one degree below the critical temperature to one degree above, whereas the relatively non-polar propylene shows a far less marked dielectric constant temperature gradient.

With regard to the second, the following observations may be made. The results are in agreement with the experiments carried out in this laboratory by Maass and co-workers (2, 11, 12, 13) on what happens above the critical temperature. They could of course have been predicted from the fact that a difference in density between gas and liquid persists above the critical temperature, and that on lowering the temperature a separation into the original composition of the medium above and below the disappearing meniscus does not take place*. The data will perhaps be useful when additional data obtained in investigations now in progress on refractive index, viscosity and solubility above the critical temperature have been accumulated.

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* *See hysteresis data in Table I.*

STUDIES IN THE SYSTEM CALCIUM-OXIDE–SULPHUR-DIOXIDE–WATER

II. CALCULATION OF IONIC CONCENTRATIONS[1]

By P. E. Gishler[2] and O. Maass[3]

Abstract

The conductivity and vapor pressure data of the system calcium-oxide–sulphur-dioxide–water presented in an earlier paper have been used to calculate ionic concentrations existing in this system, in the temperature and pressure range investigated. Two methods of calculation have been employed, one depending on the combination of vapor pressure and conductivity data, and the other, on conductivity data. For both, recourse was had to the data of Campbell and Maass on the system sulphur-dioxide–water. These methods gave results that are in good agreement with each other. The existence of a complex $CaSO_3.Ca(HSO_3)_2$ was deduced.

Hydrogen ion concentrations over the concentration and temperature range investigated have been calculated and extrapolations made to higher temperatures. These are presented in tabular form. Apart from the theoretical interest, it is pointed out that these results are of value in connection with studies of the delignification of wood by calcium-oxide–sulphur-dioxide–water solutions.

Introduction

In an earlier paper (2) a technique was described for determining vapor pressures and conductivities of the system calcium-oxide–sulphur-dioxide–water, and the data obtained were presented. Vapor pressure and conductivity values were given for a wide range of concentrations and temperatures. These values will be used in the present paper to determine hydrogen ion concentrations. Their particular interest will be discussed later on.

The system calcium-oxide–sulphur-dioxide–water can, under various conditions, contain a wide variety of compounds distributed throughout three phases. To illustrate, sulphur dioxide in the gaseous phase is in equilibrium with sulphur dioxide in the liquid phase. This is in equilibrium with sulphurous acid, which in turn is in equilibrium with its ions. On the other hand, calcium oxide combines with water to form calcium hydroxide, which is difficultly soluble in water and ionizes to some extent. Calcium hydroxide reacts with sulphur dioxide to form solid calcium sulphite. According to current ideas, calcium sulphite, virtually insoluble, forms calcium bisulphite in the presence of an excess of sulphur dioxide, calcium bisulphite existing only in solution. The complex nature of this system makes the determination of ionic concentrations difficult. In this paper only those concentrations and temperatures at which there is no solid calcium sulphite present will be considered.

The salient feature of the papers by Maass and Maass (6), Morgan and Maass (7) and Campbell and Maass (1) on the sulphur-dioxide–water equilibrium was the evidence presented to indicate that, with rise in temperature,

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sulphur dioxide in the liquid phase exists to a large extent as dissolved gas rather than as sulphurous acid, and that the higher the temperature the smaller is the amount of sulphurous acid present. As a result the apparent dissociation constant, K_a, of sulphurous acid decreases rapidly with increase in temperature although the true dissociation constant, K_3', may be only slightly altered. In any case the hydrogen ion concentration definitely decreases with rise in temperature. This property of the sulphur-dioxide–water system helps to give good qualitative explanation of the variation in conductivity of the system calcium-oxide–sulphur-dioxide–water with variation in calcium oxide concentration and temperature. To elucidate this the data of an earlier paper (2) are presented in Figs. 1 to 4.

In Fig. 1 it is seen that at 25° C. the hydrogen ion concentration at 0% calcium oxide is fairly large. The addition of calcium oxide increases the total number of ions, but reduces the number of hydrogen ions whose mobility is so much greater than that of the other ions that the addition of calcium oxide actually reduces the conductivity. With continued addition of calcium oxide the influence of the increase in the number of ions gradually predominates,

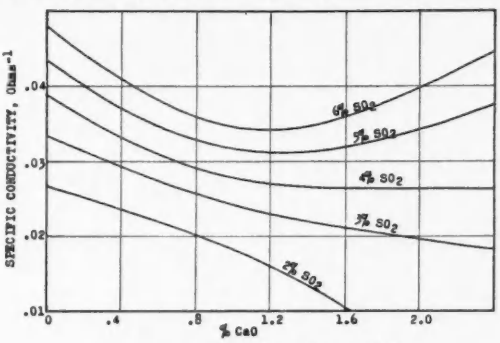


FIG. 1. *Specific conductivity—25°C.*

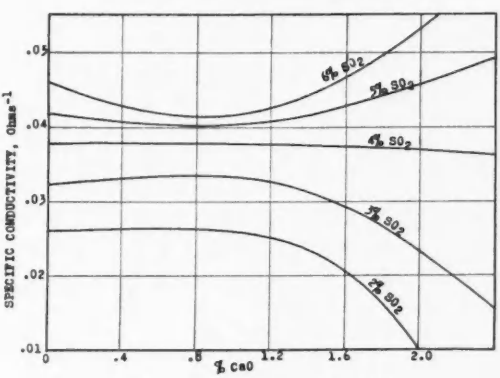


FIG. 2. *Specific conductivity—50°C.*

and therefore in the 6% and 5% sulphur dioxide curves a minimum is found. At 50° C. (Fig. 2) this minimum in the 6% and 5% curves is not so low, because at the higher temperature the initial concentration of hydrogen ions in calcium-oxide-free solution is much less. It is so much less at 70° C. (Fig. 3) and still more so at 90° C. (Fig. 4) that here the minimum disappears entirely. The reason for this is that the increase in the number of ions due to the addition of calcium oxide has the predominating influence because of the relatively fewer hydrogen ions present at the start. Furthermore, the formation of bisulphite ions due to the solution of the calcium oxide tends to decrease still further the number of hydrogen ions.

With the 4% solution, when more than 2% calcium oxide has been added the condition is reached where solid precipitates out, and, since the solid has a negative temperature coefficient, at 70° C. a maximum is reached in the conductivity values of the 4% curve. Beyond the maximum, the decrease in conductivity is due to the formation of solid which involves a reduction in the total number of ions. At the higher temperature, 90° C. (Fig. 4), this is still more pronounced. At 50° C. (Fig. 2) the 4% curve is virtually

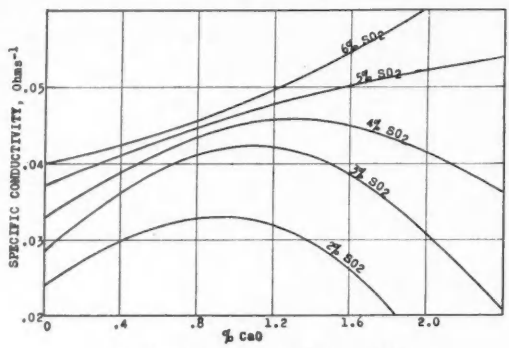


FIG. 3. *Specific conductivity—70°C.*

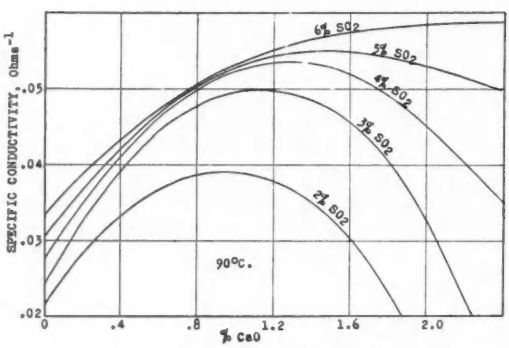


FIG. 4. *Specific conductivity—90°C.*

a straight line. To begin with, the increase in the number of ions, with the addition of calcium oxide, just compensates for the decrease in average mobility owing to the removal of hydrogen ions. Eventually in this case with continued addition of calcium oxide, precipitation of solid begins to decrease the number of ions, and at a point beyond those for which data are tabulated this curve will start to bend down, that is, show a decrease in conductivity. This is indicated in the 2% and 3% sulphur dioxide curves in this figure. It can therefore be seen that the conductivity values of the system calcium-oxide–sulphur-dioxide–water conform to the idea of decreasing hydrogen ion concentration with rise in temperature in the simpler system sulphur-dioxide–water.

It is of considerable interest to make a quantitative estimate of the magnitude of the ionic concentrations. In the first place, this will add to the knowledge of the nature of the equilibria existing in this system. In the second place, the concentration of hydrogen ions has been an important influence at higher temperatures on the physical-chemical structure of lignin. Since the system calcium-oxide–sulphur-dioxide–water is used for the delignification of wood, it is of particular interest to evaluate the hydrogen ion concentration of this system at various temperatures and under various conditions of concentration.

Hägglund and Johansson (3) have measured the rate of hydrolysis of starch, and calculated the hydrogen ion concentrations from the results of these experiments. Their results will be compared later on with those calculated by the authors.

For the calculation of the hydrogen ion concentrations from the data presented in a previous paper (2), two independent methods can be used. The first involves a combination of the vapor pressure and conductivity values. The second method depends on the information obtained from conductivities alone, provided that one takes into account the evidence, based on vapor pressure data, for the existence of a soluble calcium complex somewhat different from the commonly accepted idea of the formation of calcium bisulphite. Each method will be treated separately and then a comparison of the results will be made. The calculated hydrogen ion concentration will be discussed in connection with the role that sulphite liquor plays in the delignification of wood.

Before making any calculations a few points are worth discussing. The nomenclature used is the same as that employed by Campbell and Maass (1). Thus C_{CaO}, C_{SO_2} are the number of gram molecules of calcium oxide and sulphur dioxide respectively which are added to water to form one litre of the solution. The square brackets [ ] refer to concentrations in solution, and curved brackets ( ) are used where in the case of a divalent ion the equivalent concentration in solution is to be designated.

Part of the calculations are based on laws of equilibria which are only strictly true when the activity coefficients are unity, and as this is not the case they might be looked upon as approximations. However it may be pointed out that the results obtained are nearer the true values for the system under

investigation than might at first appear. Thus Henry's law has been found by Campbell and Maass to hold with high degree of accuracy up to 12% SO_2 solution at temperatures above 25° C. (See Fig. 7 of the paper by Campbell and Maass.) Ionic concentrations are based on conductivity measurements, and equilibrium constants calculated from them were found to hold (Campbell and Maass (1)). If the fact that they hold is fortuitous owing to compensation of two factors, nevertheless the ionic concentrations will agree with those calculated from such constants.

Calculation of Hydrogen Ion Concentrations from Vapor Pressure and Conductivity Data

According to Henry's law the partial pressure of the sulphur dioxide is proportional to the concentration of the dissolved sulphur dioxide.

$$P = K_1 [SO_2]$$

The dissolved sulphur dioxide is in equilibrium with the dissolved sulphurous acid since

$$[SO_2] [H_2O] = K_2' [H_2SO_3]$$

and

$$[SO_2] = K_2 [H_2SO_3],$$

as the concentration of the water may be regarded as virtually constant for dilute solutions. The sulphurous acid is proportional to the product of the hydrogen ion and bisulphite ion concentration, since

$$H_2SO_3 = K_3' [H^+] [HSO_3^-].$$

Consequently the partial vapor pressure of the sulphur dioxide is proportional to the product

$$[H^+] [HSO_3^-].$$

When calcium oxide is dissolved by excess sulphurous acid, the calcium complex formed, if it gives rise to bisulphite ions, will increase the amount of sulphurous acid, which in turn will increase the concentration of dissolved sulphur dioxide, and this will cause an increase in the partial vapor pressure of the sulphur dioxide. Consequently the vapor pressure of an aqueous solution of sulphur dioxide should be increased when a solution containing 1 gm. mol of calcium oxide and 2 gm. mols of sulphur dioxide is added. Therefore it is possible from considerations of vapor pressure data to evaluate solutions containing equal products $[H^+] [HSO_3^-]$, independently of the amount of calcium oxide that was added. Suppose a solution containing C_{CaO} gm. mols of calcium oxide has a vapor pressure P, then it follows that the product $[H^+] [HSO_3^-]$ in this solution has the same value as the product $[H^+] [HSO_3^-]$ of a solution containing sulphurous acid alone and having the same vapor pressure. Since the hydrogen ion concentrations of sulphurous acid solutions have been determined by Campbell and Maass (1), it is therefore possible, by having recourse to their data, to calculate the product $[H^+] [HSO_3^-]$ in a sulphurous acid solution containing dissolved lime.

Apart from the accuracy with which the vapor pressures for the solutions involved have been determined, the accuracy will depend on the validity of the relation

$$[H^+]\,[HSO_3^-] = K_3'\,[H_2SO_3].$$

Now although this relation will not hold over a wide range of concentrations when uncorrected concentrations are used, this aberration becomes of less importance when it is remembered that comparisons are made for solutions in which the products of the ionic concentrations are the same, and therefore the product $[H^+]\,[HSO_3^-]$ can be evaluated with a fair degree of certainty for those solutions for which the vapor pressure data have been determined.

The conductivity, K, multiplied by 1000 is equal to the algebraic sum of the products of the ionic concentrations and mobilities, hence,

$$1000K = \mu_{Ca^{++}}(Ca^{++})^* + \mu_{HSO_3^-}[HSO_3^-] + \mu_{H^+}[H^+]$$

where $\mu_{Ca^{++}}$ = equivalent mobility of Ca ion,
(Ca^{++}) = equivalent concentration of Ca ion,
$\mu_{HSO_3^-}$ = mobility of HSO_3 ion,
$[HSO_3^-]$ = concentration of HSO_3 ion,
μ_{H^+} = mobility of H ion
$[H^+]$ = concentration of H ion.

Furthermore

$$(Ca^{++}) + [H^+] = [HSO_3^-].$$

Since a third equation is given by

$$[H^+]\,[HSO_3^-] = S,$$

where the numerical value of S is determined from the data of Campbell and Maass (1), elimination of (Ca^{++}) and $[HSO_3^-]$ gives rise to the equation

$$(\mu_{H^+} - \mu_{HSO_3^-})\,[H^+]^2 - 1000\,K\,[H^+] + (\mu_{Ca^{++}} + \mu_{HSO_3^-})\,S = 0,$$

and

$$H^+ = \frac{1000K - \sqrt{(1000\,K)^2 - 4(\mu_{H^+} - \mu_{HSO_3^-})\,(\mu_{Ca^{++}} + \mu_{HSO_3^-})S}}{2(\mu_{H^+} - \mu_{HSO_3^-})} \qquad (1)$$

The mobilities for the hydrogen and bisulphite ions taken are those used by Campbell and Maass (1). The mobilities of the Ca ion at 25°, 50°, 70°, and 90° C. based on the International Critical Tables (4), are taken as 59.5, 90, 114 and 139 respectively.

A sample determination of (H^+) for a solution containing 1% of calcium oxide and 5% of sulphur dioxide at 50° C. is first given. The conductivity of the solution is 0.0400 (Table II, Gurd, Gishler, Maass (2)) and its vapor pressure is 75.6 cm. The concentration of a sulphurous acid solution having this vapor pressure and temperature is 3.53% (Campbell and Maass (1)). A solution having this concentration has a hydrogen ion concentration, and therefore a bisulphite ion concentration, of 0.0651, hence S has the value $(0.0651)^2$. Substituting in Equation (1), the hydrogen ion concentration is found to be 0.0236 gram mols.

* *For convenience [ ] will be used for mol concentrations, and ( ) for equivalent concentrations.*

In Table I the hydrogen ion concentrations over the range of concentrations and temperatures for which data are available, calculated by means of Equation 1, are shown.

TABLE I

HYDROGEN ION CONCENTRATIONS: VAPOR PRESSURE METHOD

% CaO	% SO_2	25°C.	50° C.	70° C.	90° C.
0	2	0.066	0.049	0.037	0.028
0	3	.081	.060	.045	.033
0	4	.095	.069	.051	.037
0	5	.109	.077	.056	.041
0	6	.122	.084	.061	.045
0.5	2	.0140	.0106	.0065	.0033
0.5	3	.0282	.0158	.0100	.0053
0.5	4	.0417	.0227	.0134	.0074
0.5	5		.0312	.0178	.0099
0.5	6		.0457	.0235	.0130
1.0	2	.0079	.0045	.0033	.00097
1.0	3	.0192	.0097	.0049	.0028
1.0	4	.0362	.0157	.0085	.0045
1.0	5		.0236	.0125	.0068
1.0	6		.0352	.0173	.0093
1.5	3	.0142	.0044	.0020	.00079
1.5	4	.0250	.0094	.0054	.0033
1.5	5	.0382	.0147	.0086	.0054
1.5	6		.0204	.0119	.0074
2.0	4	.0121	.0041	.0035	.0027
2.0	5	.0172	.0078	.0059	.0049
2.0	6	.0238	.0105	.0078	.0054

Calculation of Hydrogen Ion Concentrations from Conductivity Data

Instead of using the vapor pressures of solutions of calcium-oxide–sulphur-dioxide–water to evaluate the product $[H^+]\,[HSO_3^-]$ from Campbell and Maass's data, the relation

$$K_a = \frac{[H^+]\,[HSO_3^-]}{[SO_2] + [H_2SO_3]}$$

can be used, since the equilibrium upon which this equation is based also exists in the presence of the dissolved calcium oxide. The numerical values for K_a have been determined by Campbell and Maass (1), and it is evident from their data that within experimental error, K_a is constant at a given temperature over a wide range of concentrations. If C_{SO_2} is the number of gram mols of sulphur dioxide in the solution in which all the calcium oxide has been dissolved then

$$C_{SO_2} = [SO_2] + [H_2SO_3] + 2[Ca(HSO_3)_2] + [HSO_3^-]\,.$$

If the solution of the lime or calcium sulphite is due to the formation of calcium bisulphite then

$$Ca(HSO_3)_2 \leftrightarrows Ca^{++} + 2HSO_3^-\,.$$

The concentration of the HSO_3^- may be written

$$C_{HSO_3^-} = \alpha[HSO_3^-] + \beta[HSO_3^-],$$

where α is the fraction of the bisulphite ion associated with hydrogen ions and β the fraction associated with calcium ions, so that

$$\beta[HSO_3^-] = 2[Ca^{++}]$$

and

$$\alpha[HSO_3^-] = [H^+]$$

Furthermore

$$C_{CaO} = [Ca(HSO_3)_2] + [Ca^{++}]$$

Hence

$$\begin{aligned}[SO_2] + [H_2SO_3] &= C_{SO_2} - 2[Ca(HSO_3)_2] - \beta[HSO_3^-] - \alpha[HSO_3^-] \\ &= C_{SO_2} - 2C_{CaO} - \alpha[HSO_3^-] \\ &= C_{SO_2} - 2C_{CaO} - [H^+].\end{aligned}$$

The equation

$$K_a = \frac{[H^+][HSO_3^-]}{[SO_2] + [H_2SO_3]}$$

becomes, in the presence of lime,

$$K_a = \frac{[H^+]\{\alpha[HSO_3^-] + \beta[HSO_3^-]\}}{C_{SO_2} - 2C_{CaO} - [H^+]}$$

and this becomes

$$K_a = \frac{H^+([H^+] + 2[Ca^{++}])}{C_{SO_2} - 2C_{CaO} - [H^+]}.$$

Rearranging this we get

$$[H^+]^2 + (2[Ca^{++}] + K_a)[H^+] - (C_{SO_2} - 2C_{CaO})K_a = 0.$$

As before

$$1000K = \mu_{Ca^{++}}(Ca^{++}) + \mu_{H^+}[H^+] + \mu_{HSO_3^-}\alpha[HSO_3^-] + \mu_{HSO_3^-}\beta[HSO_3^-]$$

where

$$2[Ca^{++}] = (Ca^{++})$$

$$1000K = (\mu_{Ca^{++}} + \mu_{HSO_3^-})(Ca^{++}) + (\mu_{H^+} + \mu_{HSO_3^-})[H^+]$$

By combining the above two equations

$$[H^+]^2 + \left[\frac{1000K}{\mu_{Ca^{++}} + \mu_{HSO_3^-}} - \frac{\mu_{H^+} + \mu_{HSO_3^-}}{\mu_{Ca^{++}} + \mu_{HSO_3^-}}[H^+] + K_a\right][H^+] - (C_{SO_2} - 2C_{CaO})K_a = 0.$$

$$[H^+]^2 + \frac{1000K[H^+]}{\mu_{Ca^{++}} + \mu_{HSO_3^-}} - \frac{\mu_{H^+} + \mu_{HSO_3^-}}{\mu_{Ca^{++}} + \mu_{HSO_3^-}}[H]^2 + K_a[H^+] - (C_{SO_2} - 2C_{CaO})K_a = 0$$

$$\left(\frac{\mu_{Ca^{++}} - \mu_{H^+}}{\mu_{Ca^{++}} + \mu_{HSO_3^-}}\right)[H^+]^2 + \left(\frac{1000K + (\mu_{Ca^{++}} + \mu_{HSO_3^-})K_a}{\mu_{Ca^{++}} + \mu_{HSO_3^-}}\right)[H^+] - (C_{SO_2} - 2C_{CaO})K_a = 0$$

$$[H^+] = \frac{-\left(\frac{1000K + (\mu_{Ca^{++}} + \mu_{HSO_3^-})K_a}{\mu_{Ca^{++}} + \mu_{HSO_3^-}}\right)}{2\left(\frac{\mu_{Ca^{++}} - \mu_{H^+}}{\mu_{Ca^{++}} + \mu_{HSO_3^-}}\right)} +$$

$$\frac{\sqrt{\left(\frac{1000K + (\mu_{Ca^{++}} + \mu_{HSO_3^-})K_a}{\mu_{Ca^{++}} + \mu_{HSO_3^-}}\right)^2 + 4\left(\frac{\mu_{Ca^{++}} - \mu_{H^+}}{\mu_{Ca^{++}} + \mu_{HSO_3^-}}\right)\left(C_{SO_2} - 2C_{CaO}\right)K_a}}{2\left(\frac{\mu_{Ca^{++}} - \mu_{H^+}}{\mu_{Ca^{++}} + \mu_{HSO_3^-}}\right)} \qquad (2)$$

When Equation (2) is used to calculate ionic concentrations, the values found are less than those obtained with Equation (1). To illustrate this a few comparisons are made in Table II.

TABLE II

COMPARISION OF $[H^+]$ CALCULATED BY MEANS OF EQUATIONS 1 AND 2 FOR SOLUTIONS OF 1% CALCIUM OXIDE AND 4% SULPHUR DIOXIDE

Temp., ° C.	25	50	70	90
Equation 1	0.0362	0.0157	0.0085	0.0045
Equation 2	.0207	.0115	.0064	.0036

The differences are not very large and it would be an achievement to make it possible to evaluate the hydrogen ion concentration to this degree of accuracy above 50° C. Nevertheless, a reason for this difference can be found. Equation (2) is based on the assumption that calcium sulphite dissolves to form calcium bisulphite. If this is the case then a homogeneous liquid phase cannot be formed until the sulphur dioxide concentration is at least such that

$$2\,C_{SO_2} = C_{CaO}$$

It was observed that complete solution sometimes took place before this sulphur dioxide concentration was reached. Again if calcium bisulphite, only, is formed, the vapor pressure of solutions containing less sulphur dioxide than that given by

$$2\,C_{SO_2} = C_{CaO}$$

should be, if anything, less than that of water, whereas in the sulphur dioxide concentration range between $C_{SO_2} = C_{CaO}$ and $2C_{SO_2} = C_{CaO}$ the vapor pressures are markedly greater than those of water. This is illustrated in Fig. 5 in which the partial vapor pressures of sulphur dioxide are represented in terms of the ratio C_{SO_2}/C_{CaO}.

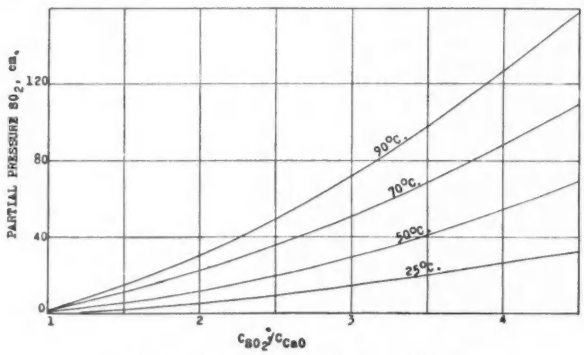
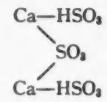


FIG. 5. *Partial pressure SO_2—1% CaO.*

From a consideration of the vapor pressures it seems obvious that a soluble complex containing a smaller amount of sulphur dioxide than is given by the ratio C_{CaO} to $2C_{SO_2}$ is formed. Since stoichiometric proportions must be retained, it is pertinent to examine the evidence of a complex depending on the ratio $1C_{CaO}$ to $1.5C_{SO_2}$. To such a complex the structural relation



might be assigned. While not advocating one way or another the fundamental basis of Langmuir's concept of the structure of the atom (5), the authors do believe that the postulates advanced by Langmuir indicate the possibility of the existence of a molecular structure, and according to Langmuir's postulates the above structure is a possible one.

A comparison of vapor pressures of solutions containing calcium oxide and sulphur dioxide in aqueous solution with those containing only sulphur dioxide in aqueous solution, can be used to determine whether the formation of the above complex is probable. For instance, using the above structure, a solution containing 0.5% of calcium oxide and 3% of sulphur dioxide at 25° C. should contain 2.14% of free sulphur dioxide. This is the vapor pressure of a 2.1% sulphur dioxide solution, as found by Campbell and Maass (1). A large number of similar cases were examined and found to conform with the above structure. A number of these are included in Table III.

TABLE III

Temp., °C.	V. p., cm.	SO_2 %
CaO—0.5%	Total SO_2—3%	Free SO_2—2.14%
25	19	2.1
50	46.5	2.1
70	88	2.08
90	140	1.93
CaO—1.0%	Total SO_2—4%	Free SO_2—2.3%
25	24	2.2
50	52	2.33
70	91	2.20
90	152	2.2
CaO—1.5%	Total SO_2—5%	Free SO_2—2.43%
25	29	2.3
50	56.5	2.6
70	105	2.6
90	180	2.8
CaO—2.0%	Total SO_2—6%	Free SO_2—2.58%
50	55	2.6
70	110	2.8
90	210	3.4

The results given cover the temperature range 25° to 90° C. and the concentration range passes diagonally across the entire range of concentrations studied. Above each section of Table III the concentration of calcium oxide and sulphur dioxide is given, together with the amount of uncombined sulphur dioxide based on a ratio $1C_{CaO}$ to $1.5C_{SO_2}$. The three columns of each section contain the temperature, the vapor pressure for the given concentration and

temperature, and finally, the concentration of sulphur dioxide required according to Campbell and Maass's (1) data to produce the vapor pressure shown in Column 2. On the basis of a 2 to 1 ratio, the amount of free sulphur dioxide would be very different, 1.86 as compared to 2.14% for a solution containing 0.5% calcium oxide and 3% sulphur dioxide; 1.83 as compared to 2.3% for a 1% calcium oxide and 4% sulphur dioxide, and so on.

There is one marked exception to the general agreement. This is found at the end of the last section (CaO 2%, SO_2 6%, at 90° C.). The free sulphur dioxide found was 3.4%, which is considerably higher than the estimated value. At the precipitation temperature there is a marked increase in the slope of the vapor pressure curve. Therefore at a concentration and temperature within the precipitation range, this relation cannot hold. This is also found, but to a lessened degree, in the section immediately above that under discussion. A discussion of the phenomenon of precipitation must be left for a later paper.

On the above evidence therefore it can be assumed that there is evidence for the formation of

$$CaSO_3 . Ca(HSO_3)_2 ,$$

and the influence of this concept on the evaluation of the hydrogen ion concentration by Equation (2) will now be shown. Without considering the matter in as great detail as that given above, the following equations may be listed.

$$C_{SO_2} = [SO_2] + [H_2SO_3] + 3[Ca_2SO_3(HSO_3)_2] + [Ca_2SO_3^{++}] + \alpha[HSO_3^-] + \beta[HSO_3^-]$$

$$C_{CaO} = 2[Ca_2SO_3(HSO_3)_2] + 2[Ca_2SO_3^{++}]$$

$$2[SO_2] + 2[H_2SO_3] = 2C_{SO_2} - 6[Ca_2SO_3(HSO_3)_2] - 2[Ca_2SO_3^{++}] - 2\alpha[HSO_3^-] - 2\beta[HSO_3^-]$$

$$[SO_2] + [H_2SO_3] = C_{SO_2} - 1.5C_{CaO} + 2[Ca_2SO_3^{++}] - \alpha[HSO_3^-] - \beta[HSO_3^-].$$

As before

$$2[Ca_2SO_3^{++}] = \beta[HSO_3^-]$$

and

$$[H^+] = \alpha[HSO_3^-].$$

Hence Equation (2) becomes

$$[H^+] = \frac{-\left(\frac{1000K + (\mu_{Ca_2SO_3^{++}} + \mu_{HSO_3^-})K_a}{(\mu_{Ca_2SO_3^{++}} + \mu_{HSO_3^-})}\right)}{\frac{2(\mu_{Ca_2SO_3^{++}} - \mu_{H^+})}{(\mu_{Ca_2SO_3^{++}} + \mu_{HSO_3^-})}} +$$

$$\frac{\sqrt{\left(\frac{1000K + (\mu_{Ca_2SO_3^{++}} + \mu_{HSO_3^-})K_a}{(\mu_{Ca_2SO_3^{++}} + \mu_{HSO_3^-})}\right)^2 + \frac{4(\mu_{Ca_2SO_3^{++}} - \mu_{H^+})}{(\mu_{Ca_2SO_3^{++}} + \mu_{HSO_3^-})}(C_{SO_2} - 1.5C_{CaO})K_a}}{\frac{2(\mu_{Ca_2SO_3^{++}} - \mu_{H^+})}{(\mu_{Ca_2SO_3^{++}} + \mu_{HSO_3^-})}} \quad (3)$$

Equation (3) is identical with Equation (2), except that $C_{SO_2} - 2C_{CaO}$ is replaced by $C_{SO_2} - 1.5C_{CaO}$, and that $\mu_{Ca^{++}}$ is replaced by $\mu_{Ca_2SO_3^{++}}$. The mobility of the $Ca_2SO_3^{++}$ ion is unknown, but there is probably little error in assigning to this ion a mobility the same as that of the calcium ion. It is

as if the calcium ion carries along with it a calcium sulphite molecule, and the assumption is that the hydration of both ions is such that the additional weight is of no material importance. In any case the mobility of the hydrogen ion is so much greater than that of the other ions that the use of the mobility of the calcium ion for the supposed $Ca_2SO_3^{++}$ ion will not introduce any large error.

It may be worth noting that the imposing appearance of Equation (3) does not mean that intricate and new ideas have been employed in its deduction. The apparently involved calculations can be considerably simplified since certain terms such as

$$(C_{SO_2}-1.5C_{CaO});\quad (\mu_{Ca_2SO_4^{++}}+\mu_{HSO_3^-})$$

etc., have constant values for certain temperatures and concentrations. However, for the presentation of the relation the replacement of such terms by constants which would then have to be defined, would not add to the simplification of its representation.

Before tabulating the values obtained for the hydrogen ion concentration as calculated by Equation (3), it should be mentioned that if the complex $CaSO_3.Ca(HSO_3)_2$ is only partially dissociated, so far as bisulphite ions are concerned, an equation identical with Equation (3) would be obtained except that the mobility of the ion $CaSO_3.Ca(HSO_3)^+$ would have to replace that of the $Ca_2SO_3^{++}$ ion.

TABLE IV

HYDROGEN ION CONCENTRATION—$C_{SO_2}-1.5\ C_{CaO}$

% CaO	%SO	25° C.	50° C.	70° C.	90° C.
0.5	2	0.0165	0.0106	0.0063	0.0039
0.5	3	.0328	.0158	.0099	.0055
0.5	4	.0511	.0238	.0141	.0091
0.5	5		.0335	.0180	.0123
0.5	6		.0465	.0229	.0155
1.0	2	.0048	.0024	.0014	.0010
1.0	3	.0191	.0099	.0051	.0031
1.0	4	.0354	.0160	.0109	.0055
1.0	5		.0233	.0123	.0077
1.0	6		.0328	.0163	.0106
1.5	3	.0060	.0033	.0018	.0010
1.5	4	.0185	.0092	.0053	.0032
1.5	5	.0282	.0148	.0085	.0055
1.5	6	.0403	.0202	.0113	.0074
2.0	4	.0064	.0038	.0022	.0014
2.0	5	.0149	.0082	.0055	.0035
2.0	6	.0232	.0097	.0074	.0055

Discussion

A comparison of the hydrogen ion concentrations as evaluated by Equations (1) and (3) shows excellent agreement at those concentrations and temperatures at which experimental data are such that this agreement might be

expected, if both equations are based on a sound foundation. This is the case with the values obtained at 50, 70 and 90° C. where concentrations are such that the solid phase is absent. This is not the case with a few 90° C. values having a relatively high CaO/SO_2 ratio. At that temperature and calcium oxide concentration, partial precipitation takes place, and, of course, with the appearance of the solid phase, Equations (1) and (3) do not hold. The question of precipitation temperatures will be dealt with in a later paper.

Apart from this, the greatest discrepancy is to be found with some of the values at 25° C. at 1.5 and 2.0% of calcium oxide concentration. With these the partial vapor pressures of sulphur dioxide are so small that the experimental error in vapor pressure determination is sufficient to account for the discrepancy. On the other hand, the conductivity values in this region are more accurate. The reverse is true at high temperatures. Consequently in weighing the relative merits of the values for hydrogen ion concentration given in Tables I and IV, greater weight should be given to those in Table I for temperatures of 70 and 90° C., whereas for temperatures of 25 and 50° C. greater weight should be given to Table IV.

It was pointed out in a previous paper (2) that the greatest extrapolation of data was made with the 0.5% calcium oxide concentration, and consequently the values for hydrogen ion concentrations deduced at that concentration will not be quite as accurate as those for the higher calcium oxide concentrations. From an experimental point of view, the data in the neighborhood of 1% CaO may be taken as the most accurate. From the data available, bisulphite ion concentration can also be calculated. This has been omitted however in order not to unduly lengthen the paper.

One of the main points of interest concerning the hydrogen ion concentrations is, as was shown in an investigation the results of which are to be published shortly, that there is an optimum hydrogen ion concentration at

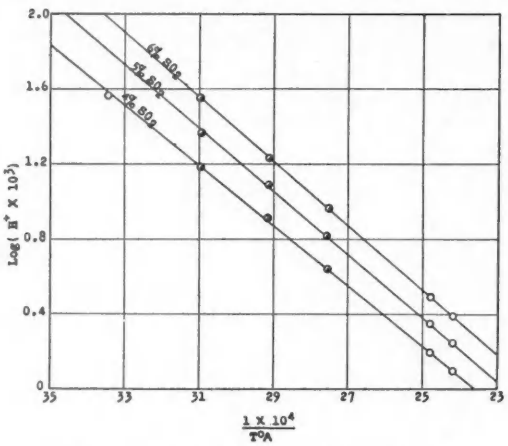


FIG. 6. *Hydrogen ion concentrations—1·0% CaO.*

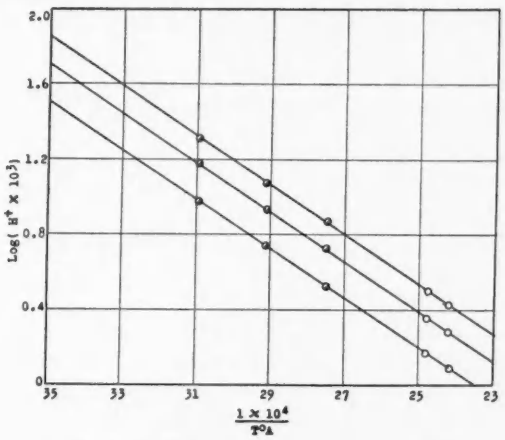


FIG. 7. *Hydrogen ion concentrations—1·5% CaO.*

which the lignin in wood when heated above 130° C. is not changed into a condition in which the delignification cannot be brought about readily by the system calcium-oxide–sulphur-dioxide–water.

The data for hydrogen ion concentrations have been established only up to 90° C. but it is possible to extrapolate by plotting log [H^+] against $1/T$. This has been done for solutions containing 4, 5 and 6% SO_2, and 1 and 1.5% CaO (Figs. 6 and 7). Between 25 and 90° C. the above relation is linear and therefore it is reasonable to expect that extrapolated values will be fairly accurate. In Table V the hydrogen ion concentrations are given at 130 and 140° C.

TABLE V

HYDROGEN ION CONCENTRATIONS—EXTRAPOLATED VALUES

	Temp., °C.	0% CaO	1% CaO	1.5% CaO
4% SO_2	130	0.020	0.0016	0.0012
	140	.017	.0013	.0010
5% SO_2	130	.022	.0025	.0022
	140	.019	.0020	.0018
6% SO_2	130	.024	.0032	.0032
	140	.021	.0025	.0027

In a paper by Hägglund and Johansson (3) to which reference has already been made, the rate of hydrolysis of starch solutions containing 5% of sulphur dioxide and 1.24 and 0.8% calcium oxide has been measured. This was carried out during the cooking of wood, over a temperature range of 60 to 130° C. It is not quite clear from their paper as to the temperature at which the hydrogen ion concentration was measured at the start of the cook, but as they mentioned that the hydrolysis of the starch was measured between 110 and 120° C. it is assumed that the hydrogen ion concentrations obtained

refer to those at that temperature. If that is the case, the values that they obtained—0.00437 for the 1.24% calcium oxide solution and 0.00479 for the 0.8% calcium oxide— compare fairly well with those calculated from the data of the authors for these concentrations at 115° C., namely 0.0033 and 0.0039 respectively.

Hägglund indicates that the evidence of Campbell and Maass for the low hydrogen ion concentration of sulphurous acid at high temperatures, and consequently the still lower hydrogen ion concentrations in the presence of calcium oxide, were not truly representative of the hydrogen ion concentration during the cooking of wood, owing to the formation of sulphonic acids. Campbell and Maass recognized this. In the presence of wood, complications such as the relatively greater absorption of free sulphur dioxide compared with that of fixed sulphur dioxide occur, as was shown by Saunderson and Maass (8).

So far as the application of the hydrogen ion concentration data established in this paper to the practical process of the delignification of wood is concerned, the obtaining of the data in this paper must be looked upon as a first step in this direction. It may be pointed out that the action of the calcium oxide is such as to produce something analogous to that of a buffer solution. The influence of sulphonic acids on the equilibria that have been discussed above is the subject of a further investigation. As the present paper has for its main object the presentation of the physical chemical equilibria that exist in the system calcium-oxide–sulphur-dioxide–water, a detailed discussion of the application of the results to the delignification of wood by sulphite liquor will be left for later papers dealing with this phase of the subject.

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